Naval Research Laboratory

Washington, DC 20375-5320

NRL/MR/6120--98-8131

Copper Sensor System for Unattended Marine Operations

R.A. LAMONTAGNE
A.M. ERVIN

Chemical Dynamics and Diagnostics Branch
Chemistry Division

K.J. EWING

Fiber Optics Technology Program
Optical Sciences Division

J.W. FOERSTER

Oceanography Department
U.S. Naval Academy
Annapolis, MD

DTIC QUALITY INSPECTED 3

January 19, 1998

19980211 042

Approved for public release; distribution unlimited.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget. Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (*Leave Blank*)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	January 19, 1998	Interim

4. TITLE AND SUBTITLE

Copper Sensor System for Unattended Marine Operations

5. FUNDING NUMBERS

PE — 62435N

6. AUTHOR(S)

R.A. Lamontagne, J.W. Foerster,* K.J. Ewing, and A.M. Ervin

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Naval Research Laboratory
Washington, DC 20375-5320

8. PERFORMING ORGANIZATION REPORT NUMBER

NRL/MR/6120--98-8131

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217-5660

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

*Oceanography Dept., U.S. Naval Academy, Annapolis, MD 21402

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (*Maximum 200 words*)

This study tests the hypothesis that the organic molecules, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (Bathocuproine (BCP)) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonic acid (Bathocuproinedisulfonic acid (BCS)) are reliable chemicals to use in developing a standard analysis procedure (BCS) and for testing an optical fiber sensor (BCP) capable of measuring copper(I) in seawater. Results show the BCS chemical provides a quick and relatively easy way to determine the concentration of copper(I) in marine and estuarine waters. Bathocuproine (BCP), once attached to optical fibers, allows for a rapid electronic measurement to quickly detect the amount and pattern of copper(I) released into the marine environment.

14. SUBJECT TERMS

Optical fiber sensor	Anti-foulant paint	Copper leach rate
Bathocuproinedisulfonic acid (BCS)	Nafion	Copper
Bathocuproine (BCP)	C_{18} resin	

15. NUMBER OF PAGES

55

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std 239-18
298-102

TABLE OF CONTENTS

Executive Summary A-1

ABSTRACT i

INTRODUCTION 1

Copper in the Environment 1
Copper Chemistry 3

ANALYTICAL METHODS 3

Chemical Procedures 4
Calibration 6
Copper Standard Preparation 6
Copper (I) Unknown Preparation 6
Probe Development 7
Testing Water 8

RESULTS AND DISCUSSION 8

Standardization Tests (Standard Method) 9
Standardization Tests (Ascorbic Acid) 9
Standardization Tests (Spectrophotometer) 10
Coupons — Source of Copper 10
Copper (I) — Leach Rate Studies 11
Probe Study 12

CONCLUSIONS 12

REFERENCES 14

Preceding Page Blank

Copper Sensor System for Unattended Marine Operations

Executive Summary

A major source of trace metal contamination in the marine environment comes from the copper containing anti-foulant paints on ship hulls. This study tests the hypothesis that the organic molecules, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (Bathocuproine=BCP) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonic acid (Bathocuproinedisulfonic acid=BCS) are reliable chemicals to use in developing a standard analysis procedure (BCS) and testing an optical fiber sensor (BCP) capable of measuring copper (I) in seawater. The purpose is to develop a sensor system that will measure trace metal contamination quickly. This will allow the deployment of remedial methods to avert an environmental problem.

Any trace metal sensor system of use in the marine environment must have

- ppb detection limits,
- in situ operation capability, and
- the ability to detect the copper (I) oxidation state.

This is important because the U.S. Navy must maintain water quality as it uses the marine environment.

Copper (I) is a potentially toxic trace metal controlled in the environment by the chemistry of the water column (pH, salinity, ligands). An anti-fouling paint containing copper (I) presents a challenge to the environment because its design is to leach continuously over a period of time. This then is a pesticide that kills or prevents attachment of organisms to a ship hull, but, also, becomes a source of introduced copper (I).

The conclusions from this study are:

- that the chemical procedure using the organic molecule, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonic acid (Bathocuproinedisulfonic acid=BCS) (the Standard Method) affords both a total and copper (I) analysis,
- that the chemical procedures are reproducible and robust,
- that the use of antifoulant paint test coupons are a good source of copper (I) for testing,
- that the leaching of copper (I) from the anti-foulant paints works best in seawater,
- that the optical fiber probe adequately reads copper (I), and
- that there is a knowledge base for continuing and expanding the copper (I) studies.

This study is the first phase in a program to develop an easily used and dependable sensor for detecting copper (I) in the environment. Field testing, testing of other polymers and probe configurations, and recommending methods to ease the copper (I) loading to the environment are necessary.

INTRODUCTION

The purpose is to develop a copper (I) sensor system for use in the marine environment. Being able to operate unrestricted in all navigable waters and maintain a world presence, is the highst prority of the U. S. Navy. International treaties and more stringent environmental laws impact on the Navy's ability to maintain a presence in the world and at home. Compliance with these treaties and laws minimizes fines and impacts operational restrictions.

The U.S. Navy uses a copper containing anti-foulant paint on the hulls of its ships. This anti-foulant paint prevents some and reduces other organisms from attaching to ship hulls. With organism attachment to a ship hull, comes increased drag and thus increased fuel consumption during passage through the water (Claisse and Alzieu 1993). In addition, fouling clogs intakes and reduces pipe diameters. This same paint is in use on commercial fleet, and on pleasure craft. Therefore, a major source of copper in the marine environment is from anti-foulant paints on ship hulls (Nriagu 1979).

This research focuses on the organic molecule, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (Bathocuproine = BCP - insoluble in water), and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonic acid (Bathocuproinedisulfonic acid = BCS - soluble in water) as reliable chemicals to use in developing an optical fiber sensor capable to measure copper (I) in the marine environment. This marine environment is not just the water adjacent to a ship hull. It is also the water upstream and downstream of the hull, the water column and the sediments. Pore water, the water in the sediment, is a large source of trace metals like copper (Nriagu 1979). Therefore, dredging operations in naval harbors can potentially re-introduce copper to the water column and create a remediation problem.

Any trace metal sensor system of use in the marine environment must have

- ppb detection limits,
- in situ operation capability, and
- the ability to detect the copper (I) oxidation state.

In this work, the concentration will be on the U.S. Navy's use of copper containing anti-foulant paints, and the rapid measurements for copper contamination in the marine aquatic environment.

Copper In the Environment

Many researchers have noted the potential toxic effects of trace metals (Sorensen 1995, Vymazal 1995, and Newman and McIntosh 1991). This report will not review the voluminous literature other than to note that the effects of copper are both beneficial and costly to plants and animals. Because copper is a biologically essential element, studying it is more difficult than a none

Manuscript approved December 1, 1997.

essential trace metal like lead or mercury. Copper remains the primary "pesticide" ingredient in anti-fouling hull paints on Navy ships. The copper leaches from the hull coating, and is a potentially toxic trace metal waste. As a toxic substance, it will eliminate aquatic biota until

- dilution,
- dissipation,
- chemical change, or
- volatilization

reduces the toxic concentrations below some population's and individual's response threshold. The result is tolerant species and/or contaminated food resources.

To understand the effect of a trace metal like copper on the biology of the water column, a comparison of normal organic matter loading to a toxic trace metal is germaine. Figure 1 illustrates the effect of a generally non-toxic waste like sewage on bottom organisms as the waste transports away from the source. Total numbers of animals decrease (solid line) in the zone of impact. After dissipation and dilution of the waste (normally the waste is oxygen consumptive), the numbers of individuals recover. The number of populations, also, reduces (dotted line) similarly but recolonization by the various species with low individual numbers, occurs more rapidly. When organic waste flows into the receiving water the function is to reduce oxygen levels. This restricts the biota to more oxygen tolerant populations until the effect decreases with distance from the source. The number of each animal in the species population takes longer to show a recovery. However, with competiion, the population diversity will return to pre-waste levels.

In Figure 2, the curves represent the effect of a toxic chemical like copper [in either Cu (I) or Cu (II) form] entering the environment. Unlike Figure 1 where some organisms exhibit a tolerance to the organic loading, here the toxic waste eliminates the bottom animals. As the waste dissipates, dilutes, chemically changes (forms organic complexes), populations (dotted line) and numbers (solid line) of organisms recover in a like manner. This is the toxic effect that copper (I) and copper (II) have on plants and animals in an aquatic environment. Bottom organisms are best reflective of either organic or toxic waste loading. In comparing the two figures (Figure 1 and 2), it is apparent that a toxic substance like copper kills the bottom animals in an area. The effect ameliorates with distance from the source as long as the input volume remains relatively constant.

Copper Chemistry

Copper has an atomic number of 29. It is the first element of subgroup IB of the periodic table, and has low chemical reactivity (towards the Nobel end of the electrochemical series), while being electronegative to hydrogen (Wakeman 1954). The electronic structure is $1s^{2}2^{2}2p^{6}3s^{2}3p^{6}3d^{10}4s^{1}$, and the $4s^{1}$

electron has a low ionization potential. This means the electron removes easily to give the cuprous ion [Cu^+ = Cu (I)]. The ionization potential of the $3d^{10}$ shell is only slightly higher resulting in the formation of the cupric ion [Cu^{++} = Cu (II)]. Standard oxidation reduction potentials (Barnard 1954) are:

$$Cu^0 \longleftrightarrow Cu^+ + e^-, -0.52\text{volts}$$
$$Cu^+ \longleftrightarrow Cu^{++} + e^-, -0.15\text{volts}$$
$$Cu^{++} \longleftrightarrow Cu^{+++} + e^-, -0.18\text{volts}$$

These potentials are important in assessing the reaction of the copper in an aqueous environment. The aqueous biogeochemistry of copper depends on

- the chemical composition and concentrations in the receiving water (calcium, magnesium, other metal species, oxygen, potassium, sodium, organics),
- the physical (pH, redox, salinity, temperature) and hydrodynamic characteristics (currents, mixing) of the receiving water,
- the chemical form of the copper in the receiving water (i.e., complexed, dissolved, solid phase, etc.), and
- the biological dynamics of the organisms in the receiving water [uptake (age, disease, size, physiology, life style), consumption, adsorption, absorption, etc.].

In general, the biogeochemistry of copper in the marine environment follows the paths outlined in Figure 3.

Figure 4 is the Global Copper cycle as reported by Nriagu (1979). Of particular interest to this program is the release and effect of copper from anti-foulant paints in the marine environment (Figure 5). The pore water of the sediments tends to be the anthropogenic sink for copper from the anti-fouling paints.

ANALYTICAL METHODS

To be an effective anti-foulant in the marine environment, copper needs to be in its ionic form (Cu (I) or Cu (II)). Copper in the ionic form is very poisonous for aquatic plant photosynthesis (Steemann Nielsen and Wium-Andersen 1970, Sunda and Guillard 1976), and aquatic animal life (Newman and McIntosh 1991, Sorensen 1995). The overall protection in the marine environment against these toxic ionic forms is the presence of organic compounds. Organic compounds (humic acids, etc.) form complexes with copper and thus remove the copper toxicity (Steemann Nielsen and Wium-Andersen 1970, Alexander and Corcoran 1967). Keeping the ionic forms available in the face of salinity, pH shifts and temperature changes is the challenge that anti-foulant paints must overcome to be economically successful. In addition, there is the challenge of copper rapidly hydrolyzing to form copper hydroxides and copper carbonates (Zirino and Yamamoto 1972).

There are a variety of methods to study copper in the aquatic environment. These include stripping voltammetry (Clavell and Zirino 1985,

Xue and Sunda 1997), atomic absorption (Zuehlke and Kester 1985, Greenberg et al 1992), inductively coupled plasma (Greenberg et al. 1992), optical fibers (Ervin et al 1993), piezoelectric sensors (Nomura et al 1997), ion-selective electrode (Vuceta and Morgan 1977), and specific dye chemistry (Bjorklund and Morrison 1997, Greenberg et al 1992, Moffett et al 1985, Diehl and Smith 1972, Blair and Diehl 1961, Borchardt and Butler 1957, Smith and Wilkins 1953) to cite some of the work. Therefore, for this study it was important to identify a simple (both in method and time), robust and reproducible procedure. In this initial study, there was 2 major parts:

a. verification of a standard wet chemical procedure, and
b. development and testing of an optical fiber probe specific for copper (I).

Chemical Procedures

The first part of this study focused on the aqueous reaction of copper (I) with an organic molecule that would develop a reproducible color in proportion to the amount of copper (I) complexed. To effect this reaction and make the measurement, we tested two methods using the primary organic reactant 2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonic acid (Figure 6) (Batho-cuproinedisulfonic acid=BCS).

The first method is the Bathocuprione Method outlined in Standard Methods (Greenberg et al. 1992). In this method, you:

- acidify a sample with hydrochloric acid,
- reduce all copper to copper (I) with hydroxylamine-hydrochloride,
- buffer the pH around 5.5 with sodium citrate, and
- react with BCS.

The BCS reaction produces an orange color that was measured on a spectrophotometer at 484nm (Figure 7). A scanning spectrophotometer (Figure 7) allows for a check on other possible contaminants, and that the reaction results are focused on the primary wavelength. According to Leckie and Davis (1979), the unique property of Cu(I) is its ability to form organometallic bonds. The Cu (I) molecule reacts with 2 BCS molecules. The BCS molecules, due to stearic hindrance, are at right angles to each other and the nitrogen molecules are exposed. Copper (I) bonds between the nitrogens and creates the orange color (Figure 8).

This method uses hydroxylamine hydrochloride (11% solution) to reduce all copper to copper (I). A buffer (sodium citrate solution @ 30%) to keep the reaction between pH 5.0-5.5, and BCS (a 0.1% solution) to complex the copper (Greenberg et al 1992). If copper (I) is present in the sample, just adding the BCS can give a measurable positive reaction. The BCS complexes copper (I) and develops color over the pH range of 3.5 to 11.0 but reacts best between pH 5.0-5.5 (Greenberg et al. 1992). Thus a method to determine both copper (I) and total copper exists.

A second analytical procedure existed and was tested against the previous "standard method". This method used a mixture of BCS (0.282 g in 500ml distilled water) and ascorbic acid (8.805 g in 500ml of distilled water). To analyze for total copper, one mixes a 50 ml sample and 50 ml of the BCS + ascorbic Acid mixture. Ionic copper (Copper (II)) reduces ascorbic acid (Cox et al 1988) and the ascorbic acid acts to stabilize the pH at a higher value (6.0-6.5). Like the "standard method" (hydroxlamine hydrochloride), this procedure reduces all copper to copper (I) and reacts with the BCS. Table 1 is a comparison of the methods.

Table 1
Comparison of the "standard method" with the ascorbic acid method.

ITEM	STANDARD METHOD	ASCORBIC ACID
DILUTION	50 ml + 16 ml of reagents	50 ml + 50 ml of reagents
SENSITIVITY (10 cm cell)	5-3000ppb	25-3000ppb
REPRODUCIBILITY	GOOD	GOOD
STANDARD CURVE	GOOD (Fig. 13)	GOOD (Fig. 13)
DETERMINE Cu (I)	GOOD	FAIR
ROBUST	GOOD	GOOD
SAMPLE VOLUME: REAGENT VOLUME	32% INCREASE	100% INCREASE

Figure 9 represents a comparison of the standard curves prepared for each method. The major problem with the ascorbic acid method is the 100% dilution that occurs when the reagents are added to the sample. This tends to weaken the color intensity in the lower ranges giving a less reliable result than the Standard Method (Figure 10). Both methods lose linearity at low ppb values, but the Standard Method curve passes through zero allowing for a more confident and reliable reading below 10 ppb. The Ascorbic Acid Method does not follow a similar path and looses reliability at 10 ppb.

Calibration

The calibration procedure involved preparing a standard curve for each method (Standard, Ascorbic Acid) in each type of water (seawater, distilled water). Known amounts of copper (I) were added in the following parts per billion (ppb=ug/L) concentrations, 5 ppb; 10 ppb; 25 ppb; 50 ppb; 100 ppb; 500 ppb; 1000 ppb. All measurements for copper were on a Hitachi scanning spectrophotometer (400 to 800nm), scan saved and peak value at 484nm recorded (Figure 7). All further testing employed standards of 50 and 100 ppb copper (I) to check on the reliability of the calibration.

Copper Standard Preparation

All testing used standard copper concentrations prepared with a 1000 ug/ml standard in 2% nitric acid from SPEX Industries, Inc. Determination of concentrations and standard curves was from data derived with a Hitachi Scanning Spectrophotometer (Figure 7).

Copper (I) Unknown Preparation

One of the goals of this study is the development of a quick analysis procedure for detecting copper (I) in seawater. Since it is difficult to keep copper (I) as copper (I) in solution, a series of experiments uses leaching copper (I) from INTERVIRON ANTI-FOULING RED PAINT (Product No. BRA640, Batch No. UUA11176E) Courtaurud Coatings, Inc. of Houston, Texas to produce Cu(I) concentrations in situ. Coating of the paint is on two types of glass coupons. The first is a glass coupon that is 75 x 25 mm (Figure 11A) which is for use in wide mouth flasks of volumes over 200 ml. Another is a smaller circular glass coupon 24 mm in diameter (Figure 11B) used in flasks with narrow mouths and volumes less than 200 ml. Before drying and coating with anti-foulant paint, all glass coupons receive soaking in dilute nitric acid and then washing and further soaking in Millipore distilled water.

The coupons are a source of copper (I) for several experiments that included:

1. leach rate studies
    - 1a. in seawater
    - 1b. in distilled water
    - 1c. in pond water
2. copper (I) to copper (II) conversion
3. leach rate under water current movement
4. probe studies

For each coupon, a measurement of the total surface area exposed in the water gave a useful value for calculating a leach rate for the amount of copper (I) released per square centimeter per hour (ug/cm^2/hr). When analyzing for copper (I) from the coupons using just the BCS reagent, all values were adjusted for the reduction in reagent volume using the conversion factor of 0.83. To simulate current movement past a hull, flasks containing the anti-foulant coated coupons were shaken gently (30 cycles per minute) on an oscillating clinical shaker.

Probe Development

Naval ships, as well as commercial and pleasure vessels, use copper containing anti-fouling paints on their hulls. These paints release over time a "pesticide," copper (I), that is toxic to organisms attempting to colonize the

vessel's hull. Since the Bathocuproine (either BCS or BCP) develops an orange color in the presence of copper (I), there is a possibility of developing an optical sensor. The sensor then can make in situ measurements of copper (I). Using this idea, the project divides into 3 major phases

- proof of concept-development and testing of a dosimeter type probe that would indicate levels of copper (I) contamination in the environment;
- improvement and perfecting probe;
- expanding sensing ability by developing a probe that is a sensor and can read both copper (I) and copper (II).

For this initial work, we concentrate on the proof of concept.

Ervin et al (1993) developed an optical sensor using immobilized BCS on an optical fiber. This work continued their initial work with an attempt to simplify the system and test it in natural seawater. This study concentrates on the initial development of a dosimeter type probe.

The probe was a 1mm C_{18} resin bead onto which BCP (water insuluable form) was immobilized. Two optical fibers (2) attached to the bead provided an incoming light source and a differential return. This return, measured by an Ocean Optics spectrophotometer at 470nm, provided a measure of copper (I) concentration.

Figure 12 is the laboratory set-up for the fiber optic probe. The fiber optic bead replaces the large probe in the beaker. A computer records the changes in bead optical density and reaction time. For this optical fiber system, a 15 minute immersion gives optimum readings.

The assembly of the optical fiber probe follows that as outlined in Ervin et al 1993. Bathocuproine (BCP) is a ligand capable of hydrophobically bonding to a C_{18} polymeric resin (Koller and Wolbeis 1991). The C_{18} polymeric resin/BCP complex is added to a solution of the perfluorinated ionomer, NAFION. The wet C_{18} resin/BCP/NAFION "glues" to the end of two optical fibers (500μm silica fiber). Figure 13 is an operational schematic of the optical fiber copper measurement system. All copper (I) and total copper concentrations used in the probe tests are from coupons soaked in natural seawater. Natural seawater is from 2000m deep in the Sargasso Sea (pH = 7.8; salinity = 35.2 ppt; temperature = 25.0°C). This is water testing free of detectable copper trace metal and filtered to remove organisms and particles larger than 0.45 microns.

Testing Water

The seawater used in all chemical procedures, leach rate studies, and for testing the probe is the same Sargasso Sea water identified earlier (center of North Atlantic Ocean gyre). This water was free of detectable copper and filtered to remove particulate organic matter. All the seawater passed through 0.45 micron Millipore cellulose filters to remove organisms and particulates. The filtering set-up used a water trap to prevent any back flushing of tap water

during filtration. Storage of the filtered water was in nitric acid cleaned bottles. Distilled water was from tap water passed through a Millipore, Inc. Milli-Q and Milli-RO deionization system and analyzed for the presence of copper. In addition, some tests used locally obtained pond water. The pond water was for use in the leach rate experiments. This water, after filtering with 0.45 micron Millipore filters, received storage in nitric acid cleaned containers.

Cleaning of all glassware was with a 10% solution of nitric acid. Distilled water rinsed glassware went into a nitric acid cleaning solution overnight, rinsed in the Millipore deionized water and soaked for 24 hours in Millipore deionized water before drying and storage. There was an on going constant check of all experimental water and glassware for contamination by copper.

RESULTS AND DISCUSSION

As described in the Methods Section, this study concentrated on the chemistry involved in two methods for measuring copper: the Standard Method (Greenberg et al 1992); and the Ascorbic Acid Method. Both methods used 2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonic acid (Bathocuproinedisulfonic acid = BCS) as the copper complexing ligand. This is a wet chemical procedure.. To develop a probe, it was necessary to use the non-water soluble ligand 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (Bathocuproine = BCP). This ligand is capable of hydrophobically attaching to a C_{18} resin bead (Ervin et al 1993) which is the beginning for developing a sensor.

Standardization Tests (standard method)

Initially, it is necessary to develop a reproducible, accurate and precise method to measure copper in the marine environment. The method must have robustness in that end products resist change over time and consistent testing yields standard curves that do not deviate. The first method is the "Standard Method" developed by Smith and Wilkins (1953) and codified by nationwide testing in the handbook *Standard Methods for the Examination of Water and Waste Water* (Greenberg et al. 1992). Figure 14 represents the curves derived from multiple testing of the "standard" method. Both distilled water and seawater testing yielded similar results.

Figure 15 presents data that show the ability of the method to read in the high ppb range. However, after 2000ppb (2ppm) the orange color is so intense that dilution is necessary to get accurate readings. Figure 15B indicates that after 2000ppb the curve tends to begin to plateau.

Treated samples kept up to 48 hours before processing show only a 5% reduction in optical density. This compares well with the data reported by Smith and Wilkins (1953) of 0.05%/hr under normal laboratory conditions (ambient air and temperature, no refrigeration, etc.) In testing for pH sensitivity, preliminary tests in seawater (35.2ppt salinity, 25°C temperature) show consistent readings

using a 1000ppb standard over the pH range of 3 to 8 (Figure 16). All adjustments of pH were with either 0.1N hydrochloric acid or 0.1N sodium hydroxide. The data compare well with that reported by Blair and Diehl (1961) between pH 3 to 10. In this study there was no measurable reaction after pH of 9. This is a preliminary test. Comparison of the curves in Figures 14, 15, and 16 demonstrates a method that:

- reads in the low ppb range,
- reads in the high ppb range,
- gives similar results in chemically different water,
- appears chemically robust, and
- produces a reasonable agreement with Beer's Law (Hemond and Fechner 1994) over concentation range of 10 - 2000ppb.

Standardization Tests (Ascorbic Acid Method)

Again the method must have robustness. The products must resist change over time, and consistent testing must yield standard curves that do not deviate. The second method is a procedure developed at the Naval Research Laboratory. It uses ascorbic acid as both a reductant and a buffer for the reaction (Ackermann and Sommer 1988). The major difference in this method compared to the Standard Method is in the volume of reagents. In the Standard method, 16ml of reagents increase the volume by 32%, while in the ascorbic acid the volume addition of reagents is 1:1 or 100% increase. For very small ppb concentrations (<25 ppb) this may create poor resolution and fluctuating readings. Figure 17 represents the curves derived from multiple testing of the ascorbic acid method. Both distilled water and seawater testing yielded similar results.

The curves in Figure 17C deviate more than the curves for the Standard Method (Figure 14C). Figure 18 compares the two methods in seawater at a salinity of 35ppt, an initial pH of 7.8 and a temperature of 25°C. The slopes are slightly different.

Figure 10 is representative of the lowest levels of detection with these methods. In the 5 to 25ppb range, the Standard Method gave reasonable results with a flatter less pronounced slope (Figure 10) and the curve intersected the X and Y axes at zero (0). The Ascorbic Acid method seemed inconsistent at these low levels (Figure 10) and did not intersect the X and Y intersect at zero (0). Both methods reached the minimum detection limit with the equipment used.

Standardization Tests (Spectrophotometer)

Figure 19 is a spectrum of curves scanned with the spectrophotometer. It is typical of all the standard curve tests and use of the spectrophotometer. The

values range from 2000ppb down to 10ppb. The curves flatten as the resolution diminishes toward the low ppb range. However, with the scanning spectrophotometer it is possible to improve the resolution and see the appropriate peak centered on 484 nm (Figure 20A,B,C). All copper (I) is in seawater at 35.2ppt, initial pH of 7.8 and at a temperature of 25°C.

Coupons - Source of Copper (I)

Copper in its ionic forms of copper (I) and copper (II) appears to quickly complex in the aquatic environment (Zirino and Yamamoto 1972, Steemann Nielsen and Wium-Andersen 1970, Alexander and Corcoran 1967). This makes providing a source of copper (I) in a relatively natural state without changing the chemistry of the water difficult. Copper containing anti-fouling paint provides the vehicle for introducing copper (I) into natural seawater. Glass coupons coated with copper containing anti-foulant paint are a source for introducing copper (I) and (II) into an experimental test procedure (Figure 21).In addition, after introducing copper (I), it is now possible to trace the conversion (oxidation) of the copper (I) to copper (II). With further addition of organic ligands, it is theoretically possible to complex the copper (I) and (II) and thus reduce its toxicity (Steemann Nielsen and Wium-Andersen 1970, Edding and Tala 1996,).

The coupons provide a source of copper (I) for

- leach rate studies in seawater, in distilled water, and in pond water
- copper (I) to copper (II) conversion
- leach rate under water current movement, and
- probe studies.

Copper (I) Leach Rate Studies

Over a 24 hour period coupons placed in 35.2 ppt salinity, a pH of 7.8 and a temperature of 25°C, leached copper (I) into the seawater. The data reveal a pattern that is one of an initial release that begins to plateau after about 16 hours (Figure 22). A second order polynomial predicts this action of plateauing.

Figure 23 is a comparison of the large rectangular coupon to the small circular coupon. There is no adjustment for surface area. The purpose in presenting the data is to confirm that the coupons are responding in a similar fashion. Both coupons release copper in a similar pattern with the smaller coupon demonstrating a more linear release.

In Figure 24, both the ascorbic acid and the standard method showed similar results but as shown in the standard curve preparation the ascorbic acid giving higher readings. The shape of the curves are interesting (Figure 24). After two hours the release of copper appears to plateau and after 4 hours the

release again increases until finally plateauing This same plateauing exists in both the large retangular and small circular coupons (Figure 25).

Studies of copper (I) release in different types of water showed that the copper containing anti-foulant paint releases best in seawater (Figure 26A and 26B). New paint that has not had immersion in seawater (Figure 26A) shows slow copper (I) release over time with very minimal releases in non-seawater. Leaching begins within the first 15 minutes of immersing the new coupon in seawater: 5 hours in pond water, and 16 hours in distilled water (Figure 26A). The data from coupons previously soaked for 24 hours in seawater gives much less reliable results though pre-immersion in seawater does aide in the release of copper (I) in no-salinity water (Figure 26B). This indicates that the anti-foulant paint used on the coupons must have seawater to trigger the copper (I) release, important to the development and testing of the probe. The probe design is for use in seawater. These coupons allow for a measurable release of copper (I) and an ability to trace the conversion of copper (I) to copper (II) (Figures 27 and 28).

Initial tests with the coupons gives an indication of the onset of conversion of copper (I) to copper (II) (Figure 27 and 28). Copper (II) begins to develop after 1 hour of immersing the anti-foulant coated coupon in seawater, after about 5 hours in pond water, and after 23 hours in distilled water (Figure 28).

Probe Study

The optical fiber probe (Figure 29) received testing in natural seawater (35ppt salinity, pH of 7.8 and a temperature of 25°C). The concept tested was that sufficient change in optical density occurred in the coated C_{18}/Nafion bead to generate a reliable measurement. Simultaneously with a probe measurement, a sample of the test water received analysis for the amount of copper (I) present.

Figure 30 is an example of a calibration curve from a probe. The optical characteristics of the small C_{18} bead are different from the cuvettes of the spectrophotometer. Therefore, instead of a linear Beers Law relationship (first order), the copper probe calibration fits a second order polynomial. In the cuvette of a spectrophotometer, the linear cell fixes in place and the reactions are complete when making measurements. The bead curves and the reaction of the copper (I) with the impregnated BCP continues. This yields a more curvilinear function. Knowing this, it is still possible to calibrate and use the sensor. The concept works and the probe yields acceptable readings.

Figure 31 is a calibration curve from a standard method procedure. The slopes of the calibration curves for Figure 30 and 31 are dissimilar but the correlation coefficients indicate a good agreement of both methods. This shows a direct dependence of optical density on the concentration of the complexed copper (I). The probe appears to read well but needs further testing in seawater both in the laboratory and in the field.

CONCLUSIONS

Copper (I) is a potentially toxic trace metal controlled in the environment by the chemistry of the water column (pH, salinity, ligands). An anti-fouling paint containing copper (I) presents a challenge to the environment because its design is to leach continuously over a period of time. This then is a pesticide that kills or prevents attachment of organisms to a ship hull, but, also, becomes a source of introduced copper (I).

The conclusions from this phase of the study are:

- that the chemical procedure using BCS (the Standard Method and the ascorbic acid method) affords both a total and copper (I) analysis,
- that the chemical procedures are reproducible and robust,
- that the anti-fouling paint coupons are a good source of copper (I) for testing,
- that the leaching of copper (I) from the anti-foulant paints works best in seawater,
- that the optical fiber probe adequately reads copper (I), and
- that there is a knowledge base for continuing and expanding the copper (I) studies.

This study is the first phase in a program to develop an easily used and dependable sensor for detecting copper (I) in the environment. Field testing, testing of other polymers and probe configurations, and recommending methods to ease the copper (I) loading to the environment are necessary.

REFERENCES

Ackermann, G., and L. Sommer. 1988. Copper . pp. 49-55. In: T.S. West and H.W. Nurnberg (ed.). *The Determination of Trace Metals in Natural Waters*. Blackwell Scientiic Publications. London. 362pp.

Alexander, J.E. and E.F. Corcoran. 1967. The distribution of Copper in Tropical Seawater. *Limnol. Oceanogr.* 12:236.

Barnard, A.J. 1954. The Simpler Inorganic Compounds of Copper. pp. 784-811. In: A. Butts (ed.). *COPPER*. Reinhold Publ. Corp. New York. 9356pp.

Bjorklund, L., and G. Morrison. 1997. Determination of Copper Speciation in Freshwater Samples through SPE-spectrophotometry. *Anal. Chim. Acta.* 343:259-266.

Blair, D. and H. Diehl. 1961. Bathophenanthrolinedisulfonic Acid and Bathocuproinedisulfonic Acid, Water Soluble Reagents for Iron and Copper. *Talanta* .7:163.

Borchardt, L.G. and J.P. Butler. 1957. Determination of Trace Amounts of Copper. *Analytical Chemistry.* 29: 414.

Claisse, D., and Cl. Alzieu. 1993. Copper Contamination as a Result of Antifouling Paint Regulations?. Marine Pollution Bulletin. 26:395-397.

Clavell, C., and A. Zirino. 1985. On-Line Shipboard Determination of Trace Metals in Seawater with a Computer-Controlled Voltametric Instrument. pp. 139-154. IN: A. Zirino (ed.). *Mapping Strategies in Chemical Oceanography.* American Chemical Society. Washington, D.C. 467pp.

Cox, B., W. Jedral, and J. Palou. 1988. Oxidation of Ascorbic Acid by Copper (II) and the Ferrocenium Ion in Acetonitrile-Water Mixtures. *J. Che. Soc. Dalton Trans*. 733-740.

Diehl, H., and G. F. Smith. 1972. *The Copper Reagents: Cuproine, Neocuproine, Bathocuproine.* G. Frederick Smith Chem. Co. Columbus, Oh. 43pp.

Edding, M., and F. Tala. 1996. Copper Transfer and Influence on a Marine Food Chain. *Bull. Environ. Contam. Toxicol*. 57:617-624.

Ervin, A., K. Ewing, R. Lamontagne, I. Aggarwal and D. Rowley. 1993. Development of a Fiber-optic Sensor for Trace Metal Detection in Aqueous Environments. *Applied Optics*. 32:4287-4290.

Ervin. A.1995. *Investigations of Cu(I) Reactions with 2,9-Dimethyl-4,7-Diphenyl-1,10-Phenanthroline Towards Metal Ion Detection.* Doctoral Dissertation. George Washington U. 214pp.

Greenberg, A., L. Clesceri, and A. Eaton. 1992. *Standard Methods for the Examination of Water and Wastewater.* 18th Ed. APHA. Washington D.C.

Hemond, H, and E. Fechner. 1994. Chemical Fate and Transport in the Environment. Academic Press, Inc. San Diego CA. 338pp.

Koller, E., and O. Wolfbeis. 1991. Sensor Chemistry. pp.303-323. In: O. Wolfbeis (ed.). Fiber Optic Chemical Sensors and Biosensors. CRC Press. Boston.

Leckie, J. O. and J.A. Davis III. 1979. Aqueos Environmental Chemistry of Copper. pp. 89-121. IN: Nriagu, J. O. (ed.). *Copper in the Environment. Part I: Ecological Cycling*. John Wiley and Sons, Inc. New York. 522pp.

Mackenthun, K.M. 1969. *The Practice of Water Pollution Biology*. U.S. Dept. of the Interior. Fed. Wat Poll. Control Adm. Div. Technical Support. 281pp.

Moffett, J., R. Zika, and R. Pentasne. 1985. Evaluation of Bathocuproine for the Spectrophotometric Determination of Copper (I) and Copper Redox Studies with Applications in Studies of Natural Waters. *Anal. Chim. Acta.* 175:171-179.

Newman, M.C., and A.W. McIntosh. 1991. *Metal Ecotoxicology*. Lewis Publ. Boca Raton Fl. 399pp.

Nomura, T., M. Kumagai, and A. Sato. 1997. Adsorptive Determination of Copper (II) in Solution as Its N,N-diethyldithiocarbamate on an Electrode-Separated Piezoelectric Quartz Crystal. *Anal. Chem. Acta.* 343:209-213.

Nriagu, J. O. (ed.) 1979. Copper in the Environment. Part I: Ecological Cycling. John Wiley and Sons, Inc. New York. 522pp.

Smith, G.F., and D.H. Wilkins. 1953. A New Colorimetric Reagent Specific for Copper. *Anal. Chem.* 25:510.

Sorensen, E.M.B. 1991. *Metal Poisoning in Fish.* CRC Press. Boca Raton Fl. 374pp.

Steemann-Nielsen, E. and S. Wium-Anderson. 1970. Copper Ions as Poisions in the Sea and Freshwaters. *Mar. Biol.* 6:93.

Sunda, W.G., and R.R. Guillard. 1976. The Relationship between Cupric Ion Activity and the Toxicity of Copper to Phytoplankton. *J. Marine Research.* 34:511-529.

Vuceta, J. and J.J. Morgan. 1977. Hydrolysis of Cu(II). *Limnol. Oceanogr.* 22:742

Vymazal, J. 1195. *Algae and Element Cycling in Wetlands* . CRC Press, Inc. Boca Raton Fl. 689pp.

Wakeman, D.W. 1954. The physical chemistry of copper. pp. 417-446 IN: A. Butts. *COPPER.* Reinhold Publ. Corp. New York. 9356pp.

Xue, H., and W. Sunda. 1997. Comparison of Cu (II) Measurements in Lake Water Determined by Ligand Exchange and Cathodic Stripping Voltammetry and Ion-Selective Electrode. *Environ. Sci. Technol.* 31:1902-1909.

Zirino, A. and S. Yamamoto. 1972. A pH Dependent Model for the Chemical Speciation of Copper, Zinc, Cadmium and Lead in Seawater. *Limnol Oceanog* 17:661-671.

Zulke, R., and D. Kester. 1985. Development of Shipboard Copper Analyses by Atomic Absorption Spectroscopy. pp. 117-137. *Mapping Strategies in Chemical Oceanography.* American Chemical Society. Washington, D.C. 467pp.

FIGURE CAPTIONS

Figure 1. Organic (non-toxic) waste effects on bottom biota (redrawn from Mackenthun 1969).

Figure 2. Toxic waste effects on bottom biota (redrawn from Mackenthun 1969).

Figure 3. Ocean copper cycle (data from Nriagu 1979).

Figure 4. Global copper cycle (redrawn from Nriagu 1979).

Figure 5. Anthropogenic sources and the major sink for copper in the marine environment. T= metric tons. (data from Nraigu 1979).

Figure 6. Bathocuproinedisulfonic acid (BCS) and Bathocuproine (BCP) used for measuring Copper (I). The BCS is used in the "wet" chemistry procedure as it is water soluble, while water insoluble BCP is used for the probe (molecules redrawn from Diehl and Smith 1972).

Figure 7. Set-up for measuring the results of the copper (I) reaction.

Figure 8. Copper (I) complexed between the nitrogens of BCS molecules that are at right angles to each other.

Figure 9. Comparison of the "standard method" and the ascorbic acid method in both seawater at pH=7.8, salinity=35.2, and temperature=25°C and distilled water at pH=6.6, salinity=0, and temperature=25°C.

Figure 10. Test of reliability to measure low concentrations of copper (I) between methods. In replicate samples the Standard Method procedure appears more reliable below 10 ppb.

Figure 11. Glass coupons with red anti-fouling paint coating. **A**. Larger coupon used for wide mouth flasks and volumes over 200 ml. **B**. Smaller coupons used for narrow mouth flasks of volumes less than 200 ml. The anti-fouling paint is a source of copper (I).

Figure 12. Laboratory set-up of the probe system. (A) = spectrophotometer; (B) uncoated C_{18} resin bead; (C) resin bead coated with immobilized BCS; (D) BCS on resin bead after reacting with copper (I).

Figure 13. Operational schematic of the fiber optic metal detection system.

Figure 14. Standard Method for measuring copper. A. is the result in distilled water; B. is the result in seawater; C. is the comparison of the results in two chemically different media, distilled water (pH = 6.8, salinity = 0, temperature =25°C) and seawater (pH = 7.8, salinity = 35.2 ppt, temperature = 25°C).

Figure 15. The upper limits of the Standard Method in seawater. A.= a normal linear regression shows the standard curve representing a wide range of concentrations. B.= a curvilinear regression actually fits the points better showing the tendency for the curve at the higher concentrations to plateau.

Figure 16. The pH range over which all copper is converted to copper (I) in this study.

Figure 17. Ascorbic Acid method for measuring copper. A. is the result in distilled water; B. is the result in seawater; C. is the comparison of the results in two chemically different media, distilled water (pH = 6.8, salinity = 0, temperature =25°C) and seawater (pH = 7.8, salinity = 35.2 ppt, temperature = 25°C).

Figure 18. Comparison of the Standard Method (black triangles) to the Ascorbic Acid Method (open squares) at the low level of detection.

Figure 19. Scanning spectrophotometer plots of Copper (I) concentrations from 10 to 2000ppb.

Figure 20. Individual plots of the various concentrations demonstrate a similar peak centered at 484nm. Optical density resolution increases with the lower concentrations (B and C).

Figure 21. Experimental glass coupons coated with copper containing anti-fouling paint.

Figure 22. Leaching experiment using copper containing anti-fouling paint on glass coupons placed in 35.2ppt salinity seawater, at a pH of 7.8, a temperature of 25°C and a slow shaking rate of 30 cycles per minute.

Figure 23. Comparison of the copper leaching from the large rectangular and smaller circular coupons.

Figure 24. Comparison of the Ascorbic Acid Method and the Standard Method for use in profiling and analyzing the leach rate of copper (I) from anti-foulant paint.

Figure 25. Comparison of the release of copper from the rectangular and circular coupons. Both types of coupons show the plateauing between 2 and 4 hours (boxed area).

Figure 26. Comparison of the leaching of copper (I) into three different types of water. Seawater and pond water with natural organic and inorganic ligands, and distilled water with no ligands. A.= results of new coupons not previously seasoned in seawater. B.= results of coupons previously seasoned in seawater for 24 hours.

Figure 27. Copper (II) developing in the three test waters.

Figure 28. The copper (I) to copper (II) conversion in seawater. Copper (I) is from glass coupons coated with copper containing anti-fouling paint.

Figure 29. The principle of the probe reacting to copper (I). The bead turns orange as it absorbs copper (I). Optical density measured at 470nm.

Figure 30. Calibration curve for the fiber optical copper sensor.

Figure 31. Calibration curve for the Standard Method procedure using a 10cm cuvette at 484nm in a spectrophotometer.

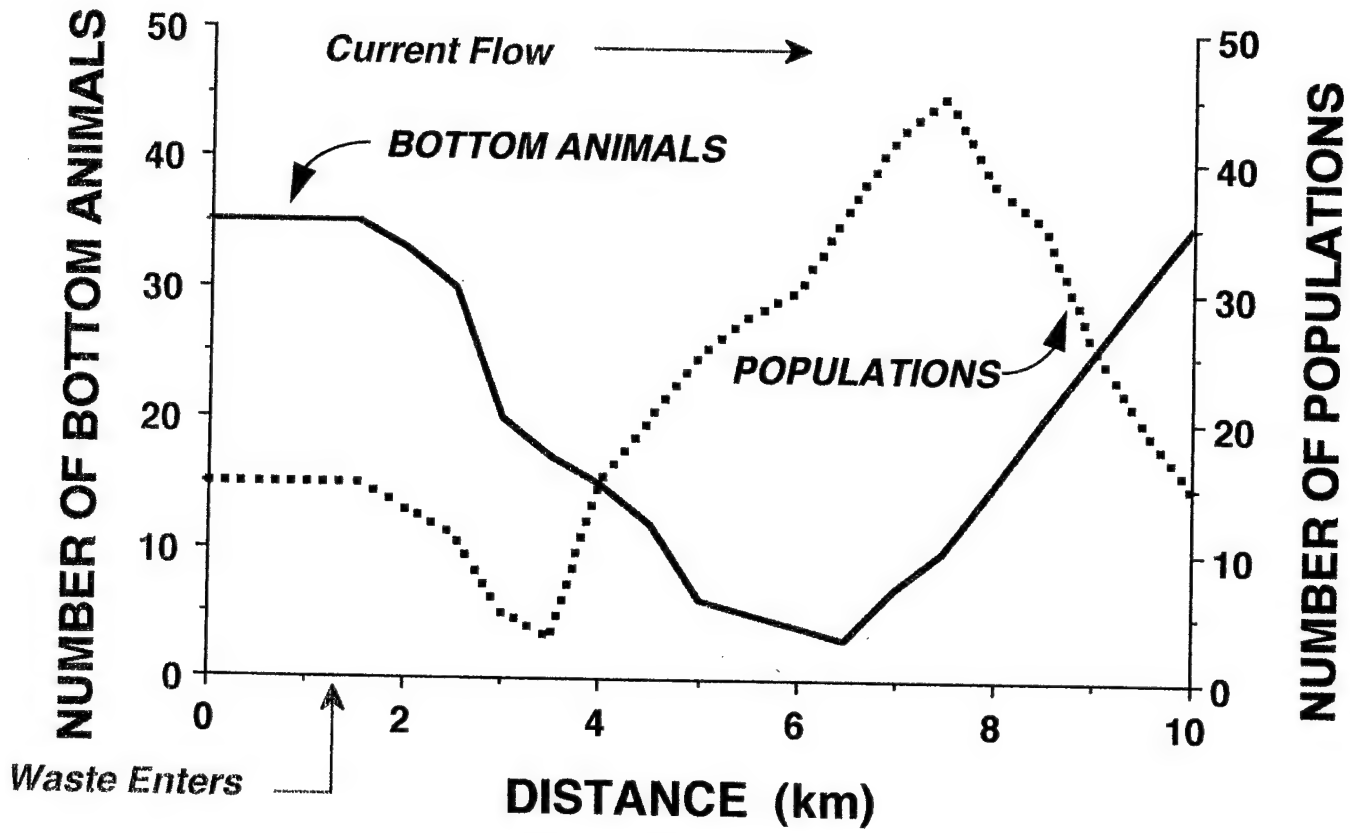

Current Flow
BOTTOM ANIMALS
POPULATIONS
Waste Enters
NUMBER OF BOTTOM ANIMALS
NUMBER OF POPULATIONS
DISTANCE (km)
0
10
20
30
40
50
0
2
4
6
8
10

Figure 1.

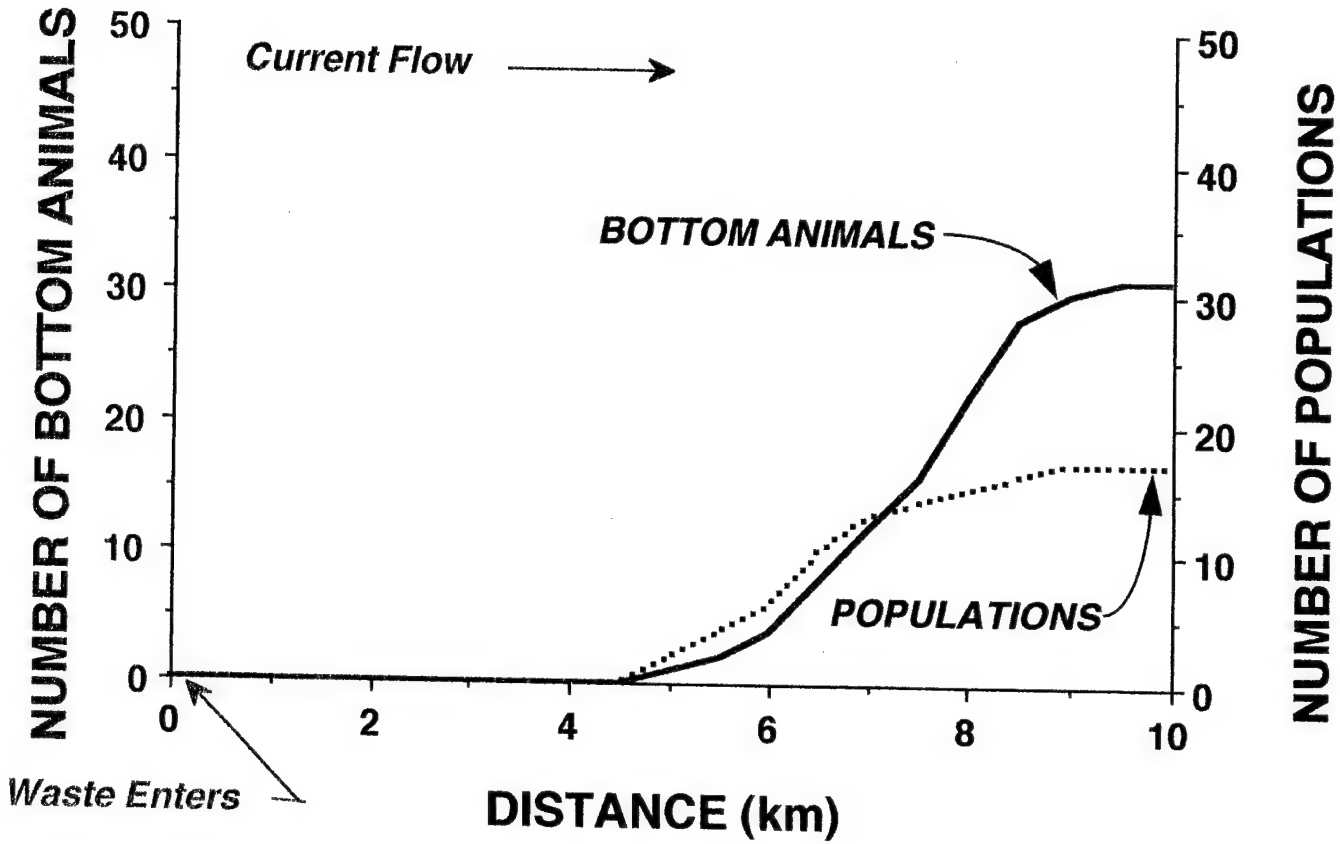

NUMBER OF BOTTOM ANIMALS
50
40
30
20
10
0
Current Flow
BOTTOM ANIMALS
POPULATIONS
0
2
4
6
8
10
Waste Enters
DISTANCE (km)
50
40
30
20
10
0
NUMBER OF POPULATIONS

Figure 2.

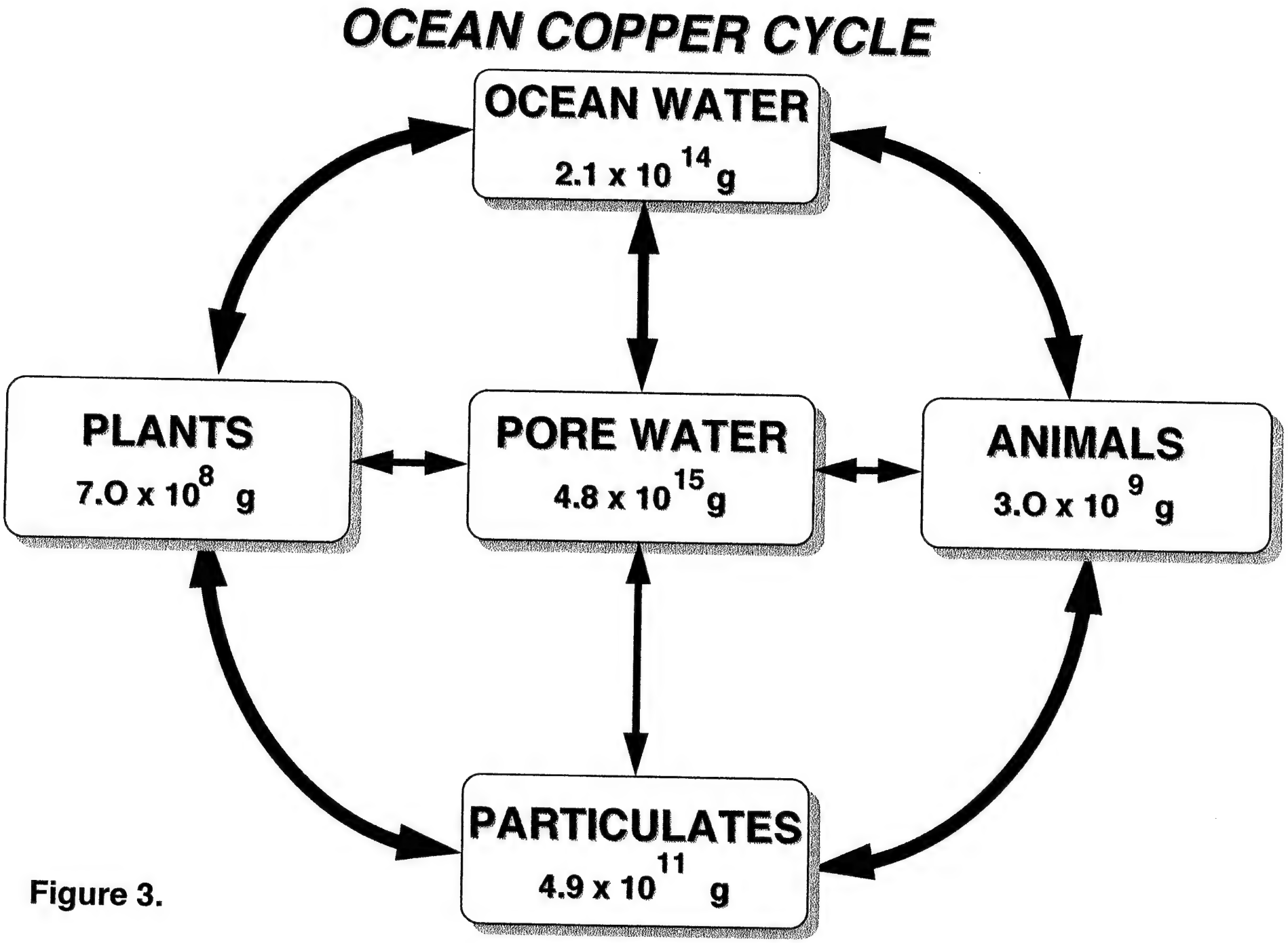

OCEAN COPPER CYCLE
OCEAN WATER
2.1 x 10 14 g
PLANTS
7.0 x 10 8 g
PORE WATER
4.8 x 10 15 g
ANIMALS
3.0 x 10 9 g
PARTICULATES
4.9 x 10 11 g

Figure 3.

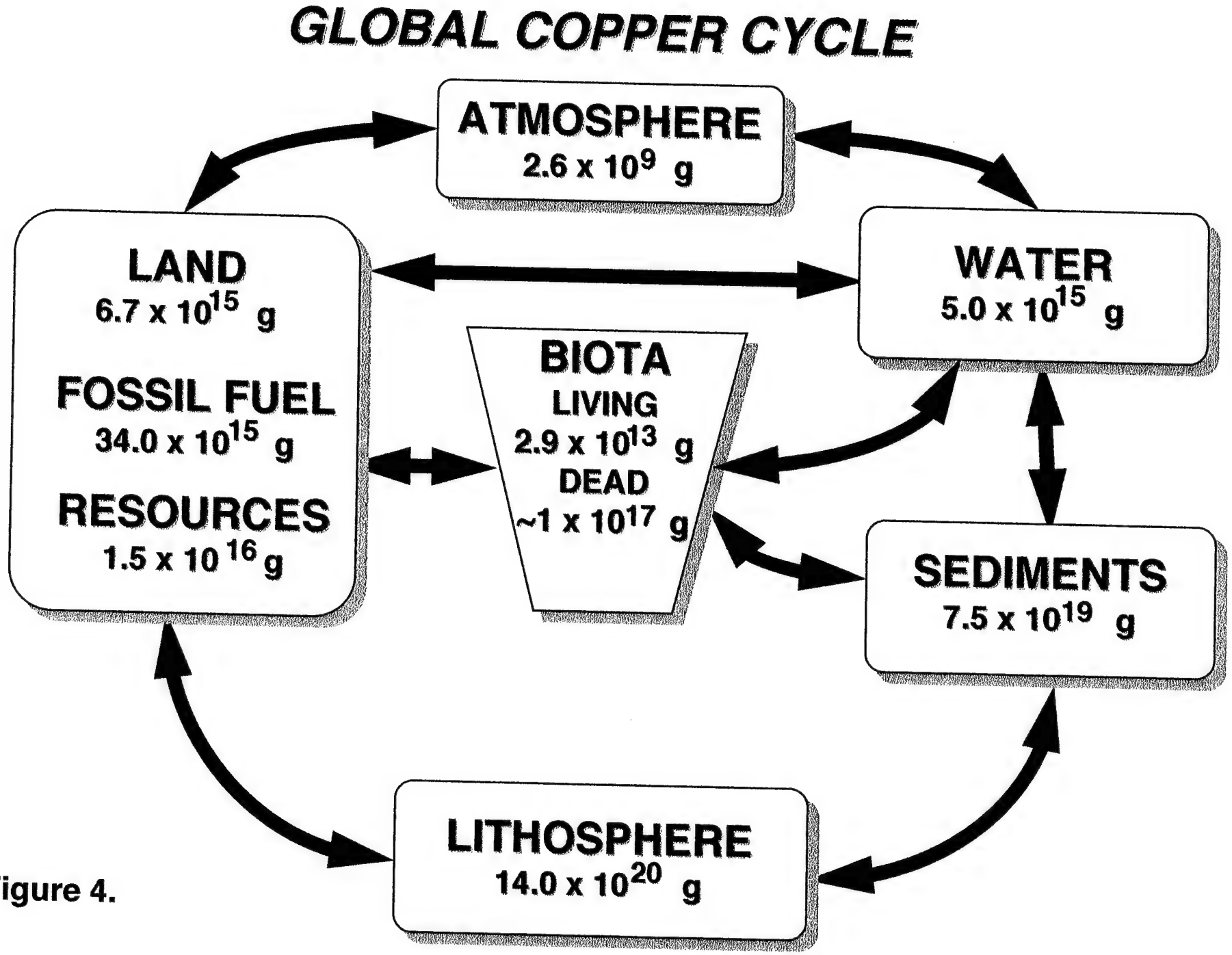

GLOBAL COPPER CYCLE
ATMOSPHERE
2.6 x 10^9 g
LAND
6.7 x 10^15 g
FOSSIL FUEL
34.0 x 10^15 g
RESOURCES
1.5 x 10^16 g
WATER
5.0 x 10^15 g
BIOTA
LIVING
2.9 x 10^13 g
DEAD
~1 x 10^17 g
SEDIMENTS
7.5 x 10^19 g
LITHOSPHERE
14.0 x 10^20 g

Figure 4.

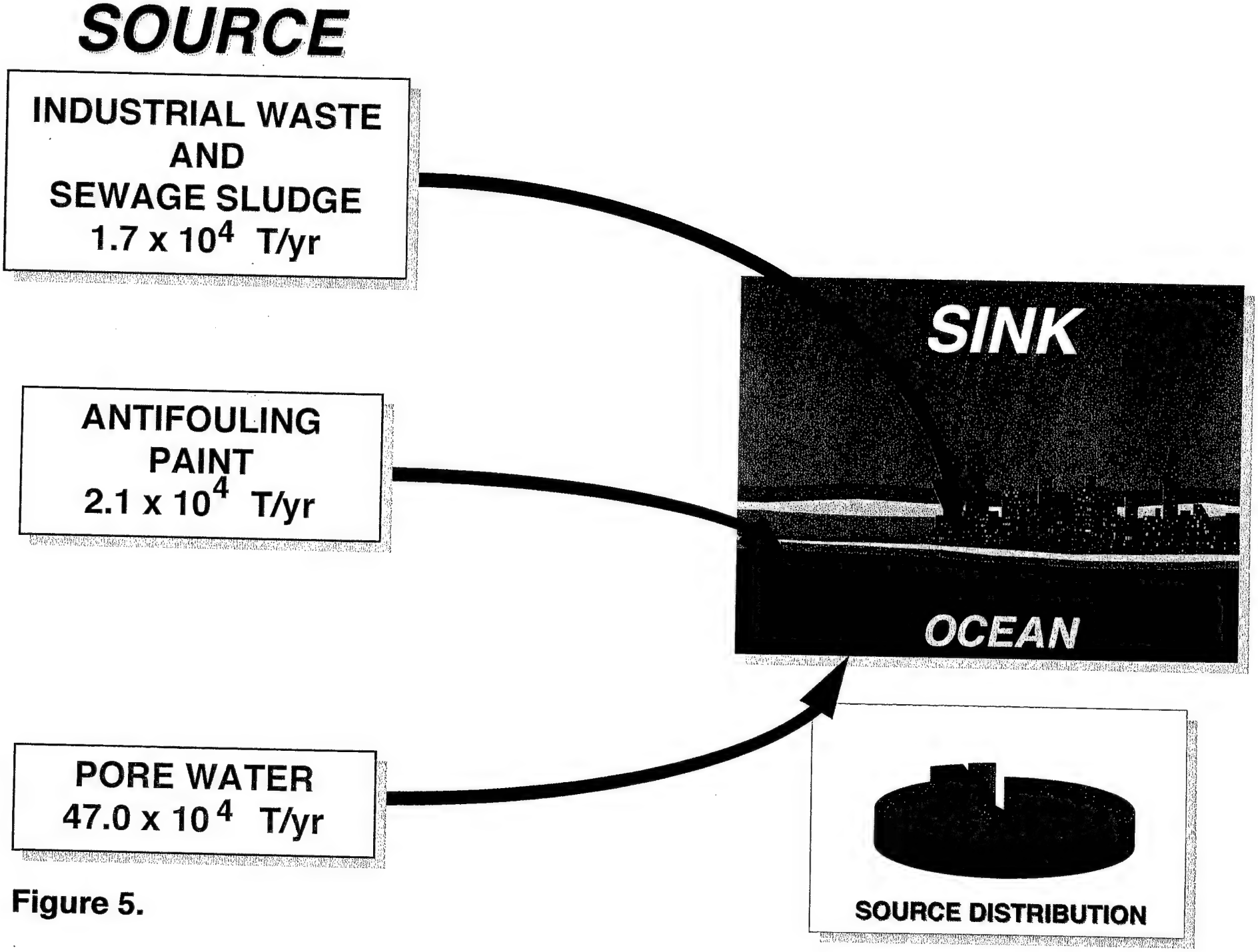
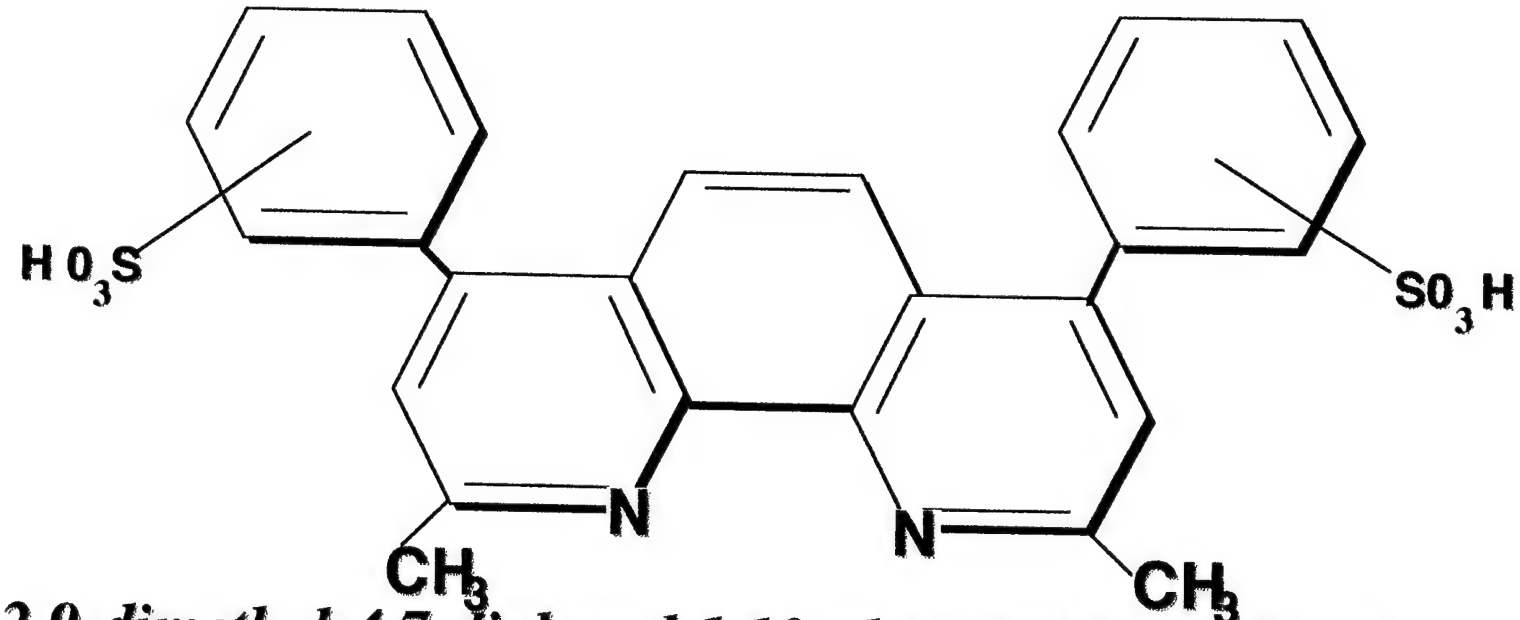

SOURCE
INDUSTRIAL WASTE
AND
SEWAGE SLUDGE
1.7 x 10^4 T/yr
ANTIFOULING
PAINT
2.1 x 10^4 T/yr
PORE WATER
47.0 x 10^4 T/yr
SINK
OCEAN
SOURCE DISTRIBUTION

Figure 5.



2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonic acid

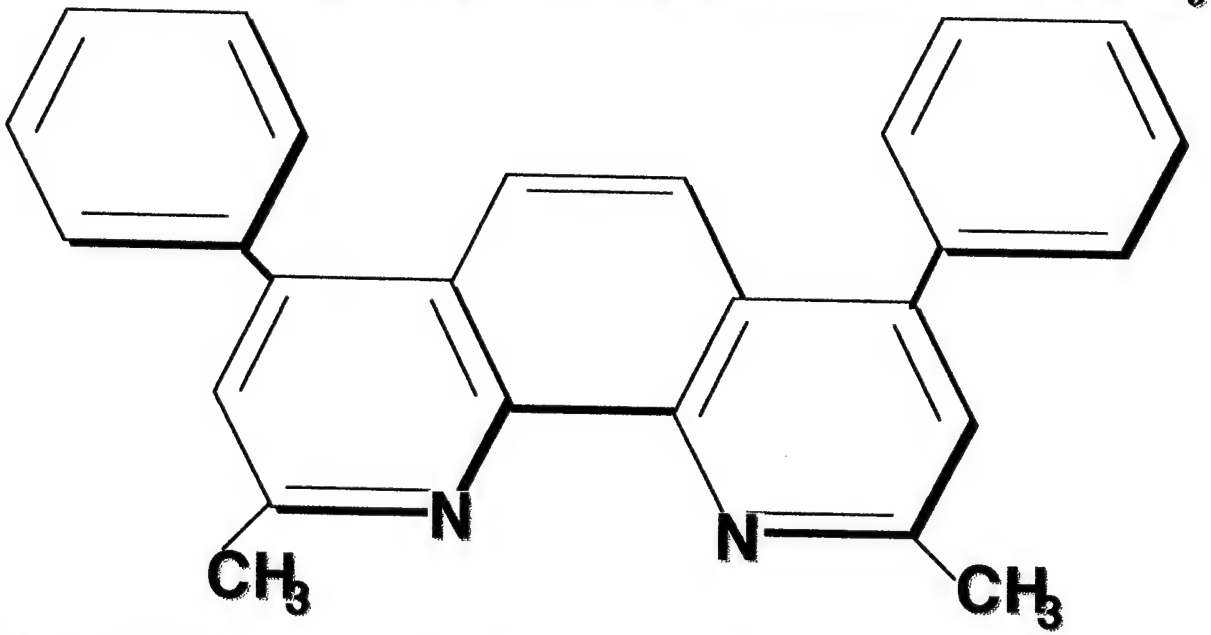


Figure 6. *2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline*

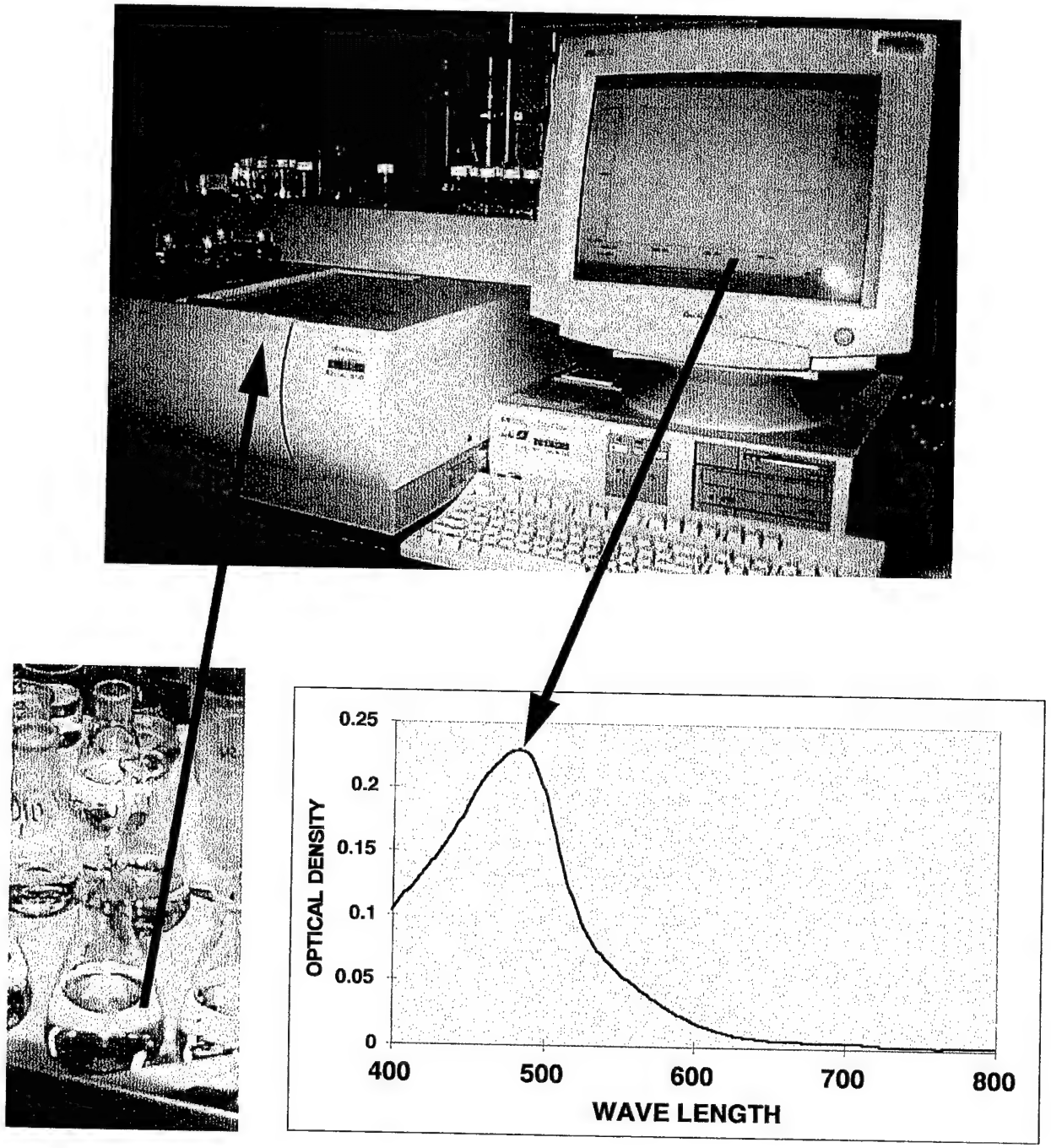

OPTICAL DENSITY
0.25
0.2
0.15
0.1
0.05
0
400
500
600
700
800
WAVE LENGTH

Figure 7.

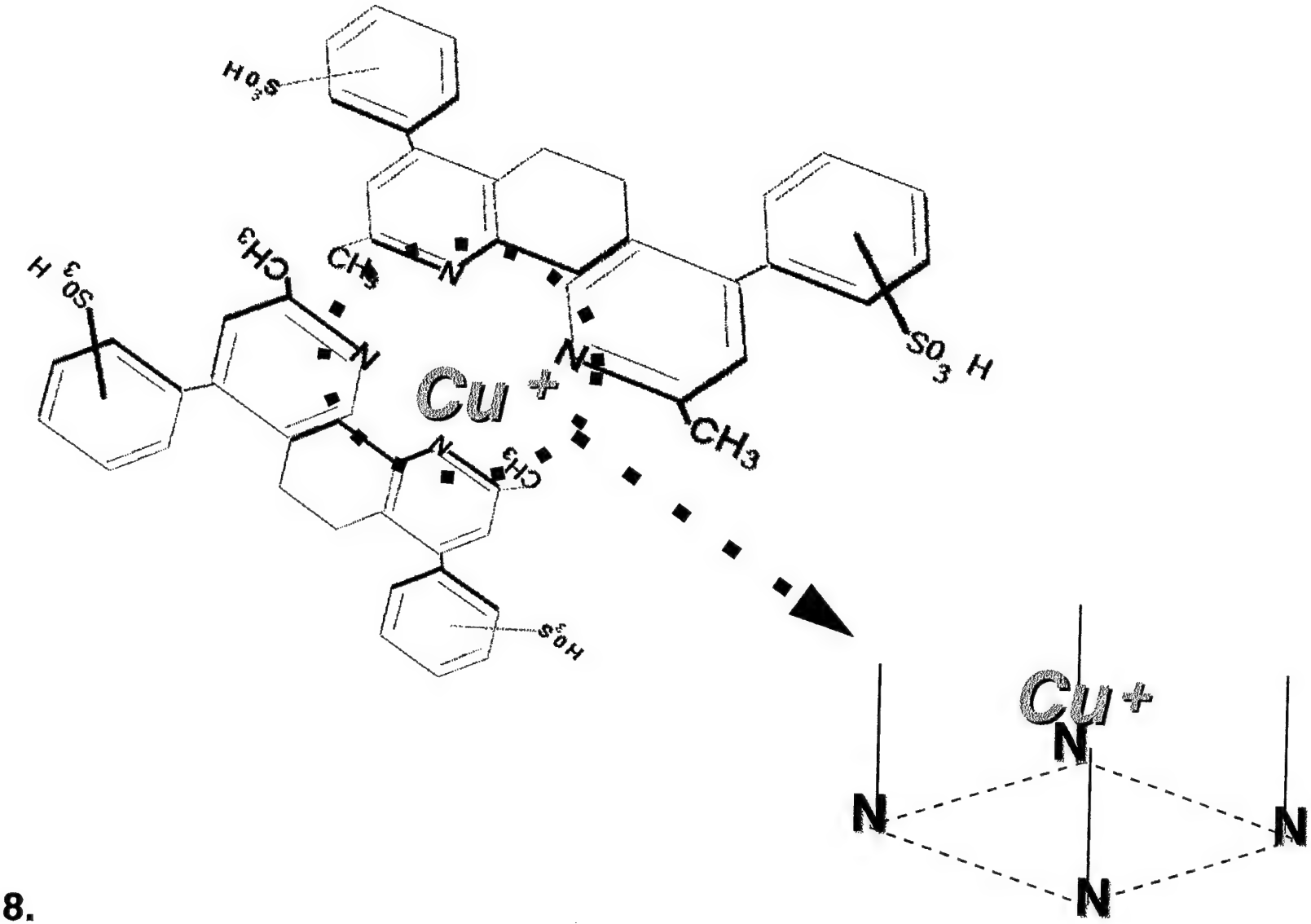


Figure 8.

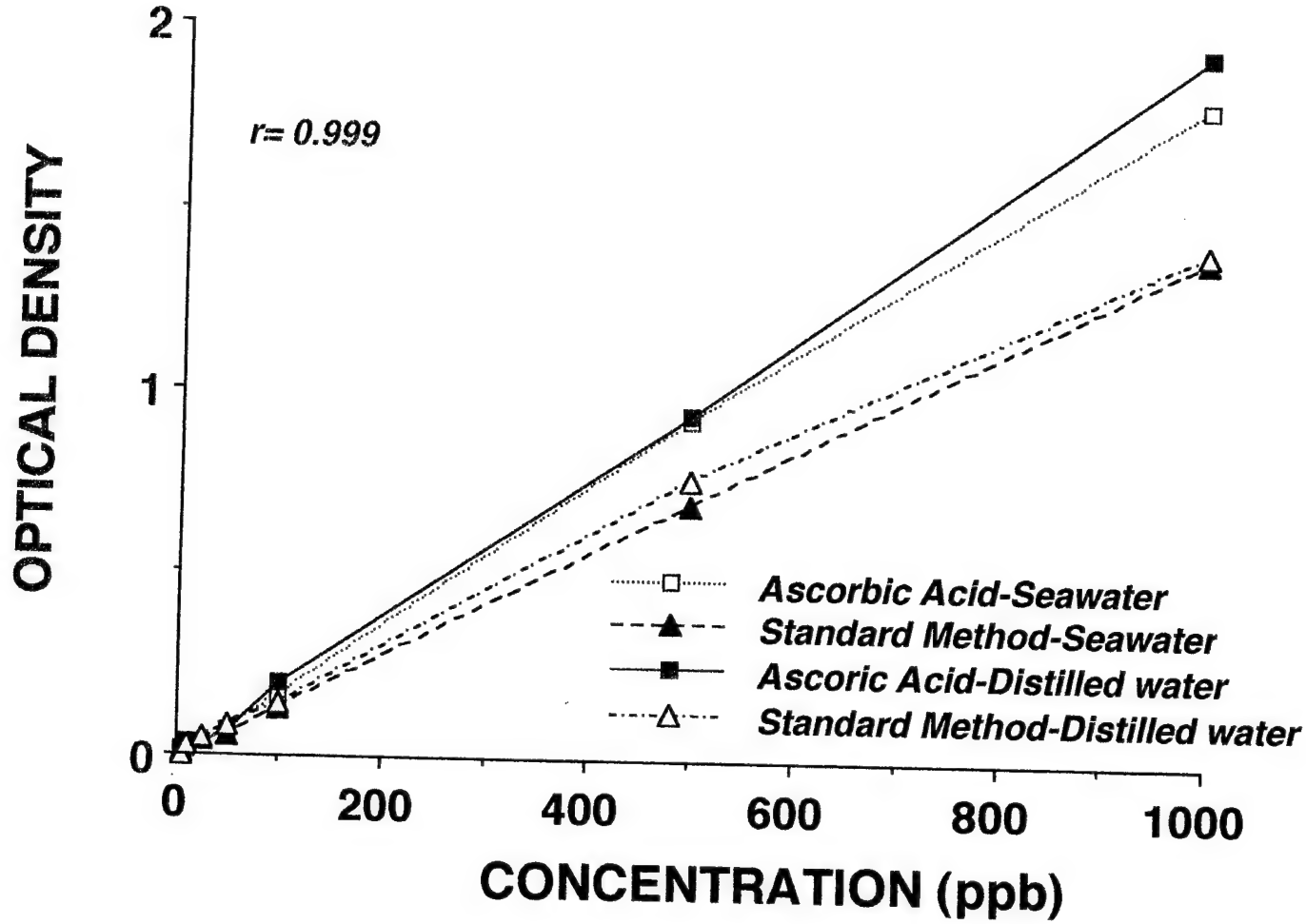

OPTICAL DENSITY
2
1
0
r= 0.999
Ascorbic Acid-Seawater
Standard Method-Seawater
Ascoric Acid-Distilled water
Standard Method-Distilled water
0
200
400
600
800
1000
CONCENTRATION (ppb)

Figure 9.

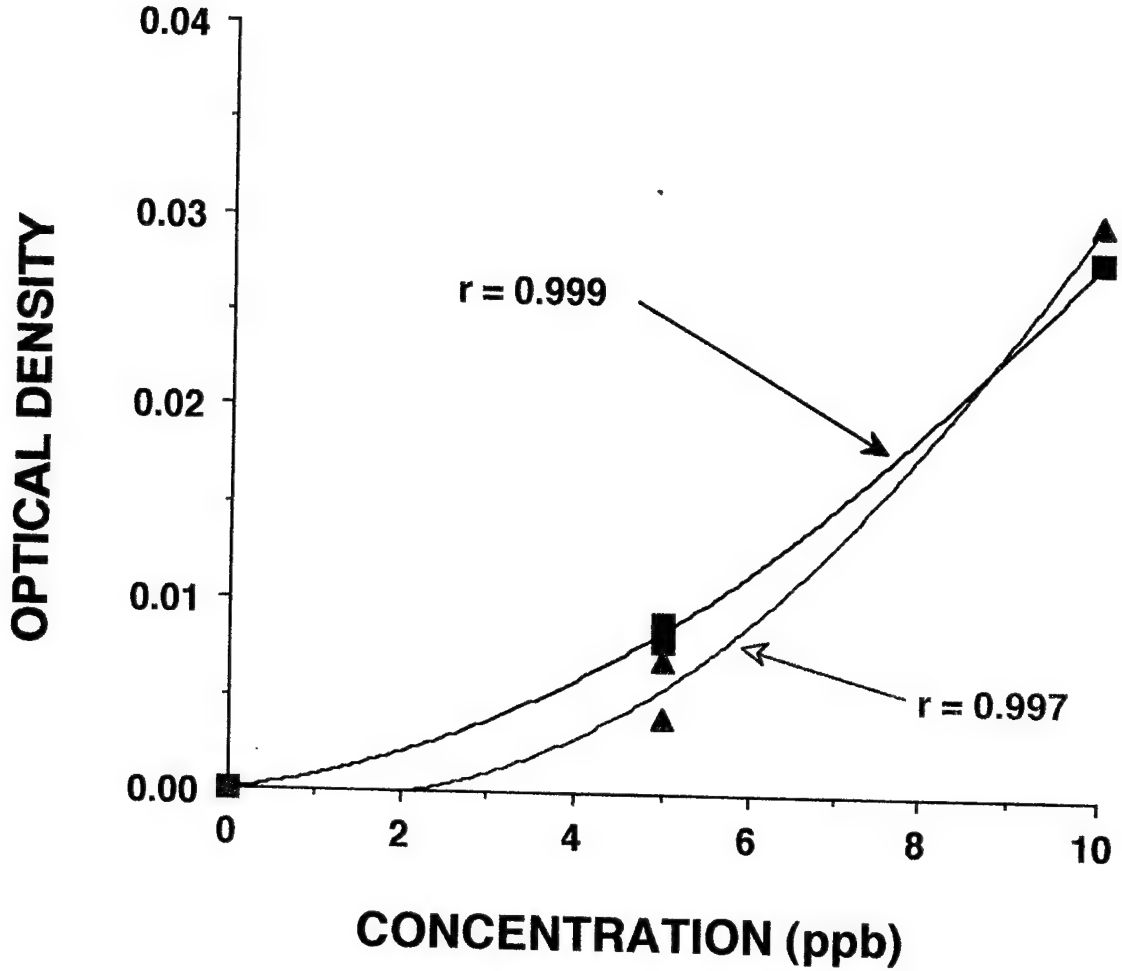
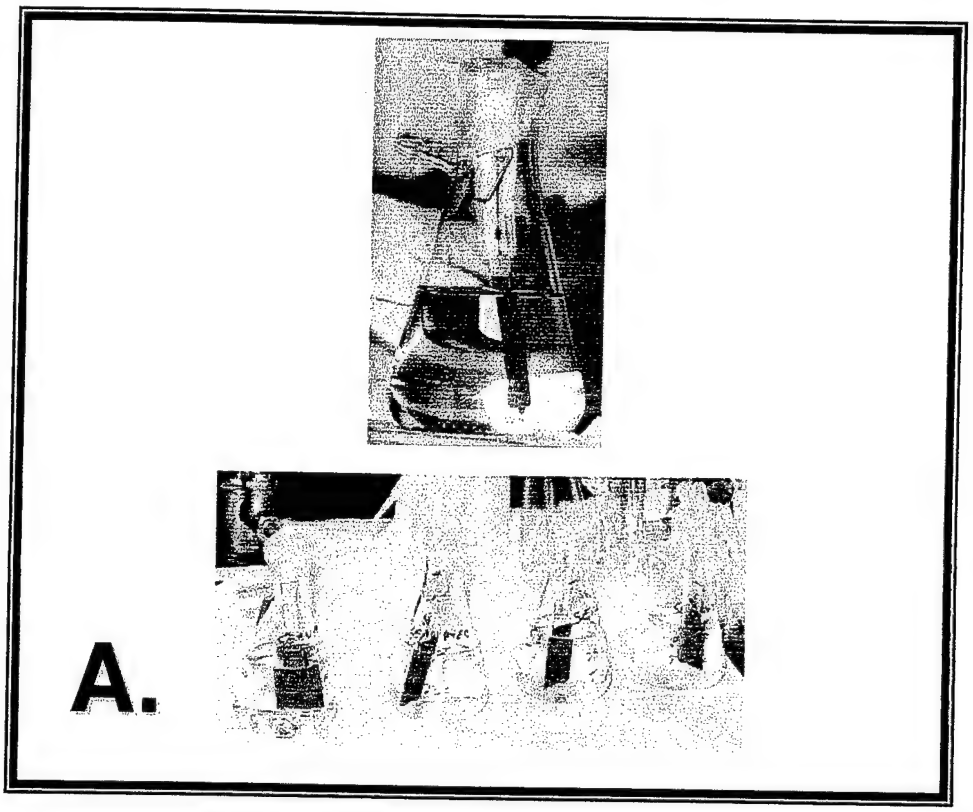

0.04
0.03
0.02
0.01
0.00
OPTICAL DENSITY
r = 0.999
r = 0.997
0
2
4
6
8
10
CONCENTRATION (ppb)

Figure 10.



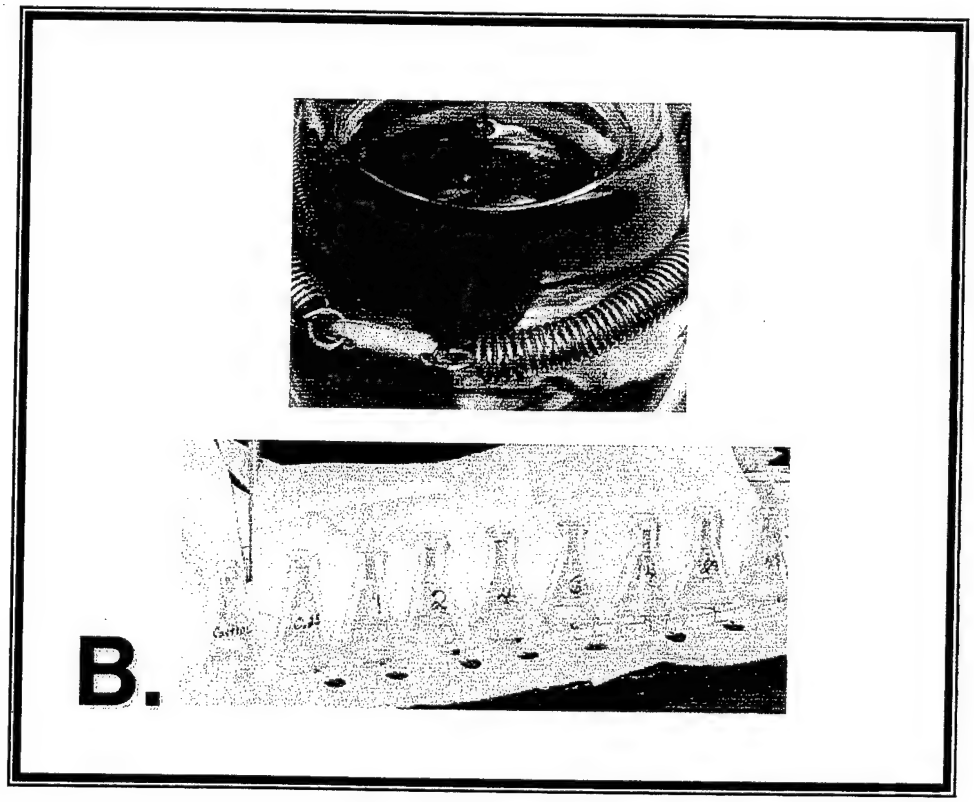


Figure 11.

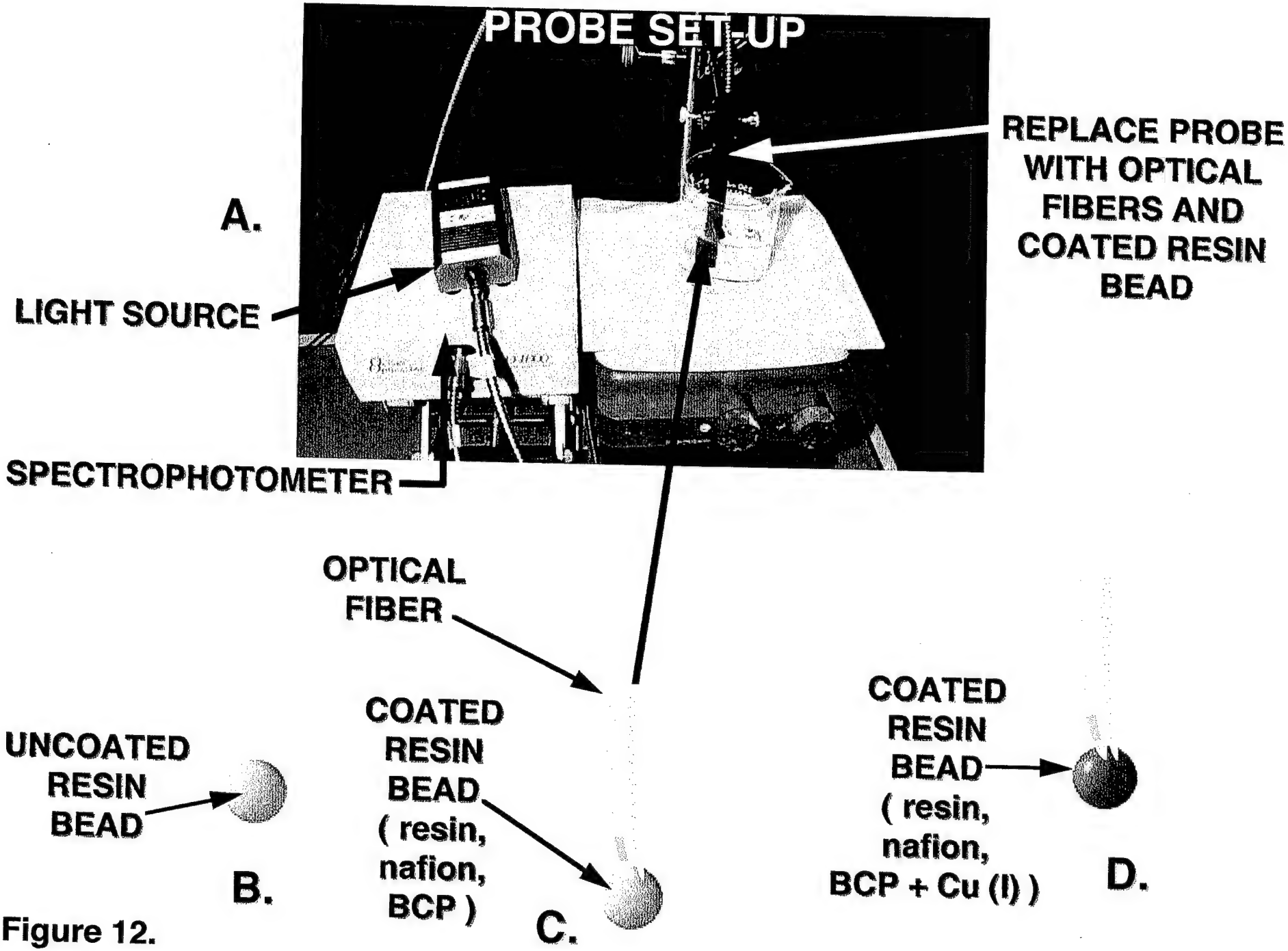

PROBE SET-UP
A.
LIGHT SOURCE
SPECTROPHOTOMETER
REPLACE PROBE WITH OPTICAL FIBERS AND COATED RESIN BEAD
OPTICAL FIBER
UNCOATED RESIN BEAD
B.
COATED RESIN BEAD (resin, nafion, BCP)
C.
COATED RESIN BEAD (resin, nafion, BCP + Cu (I))
D.

Figure 12.

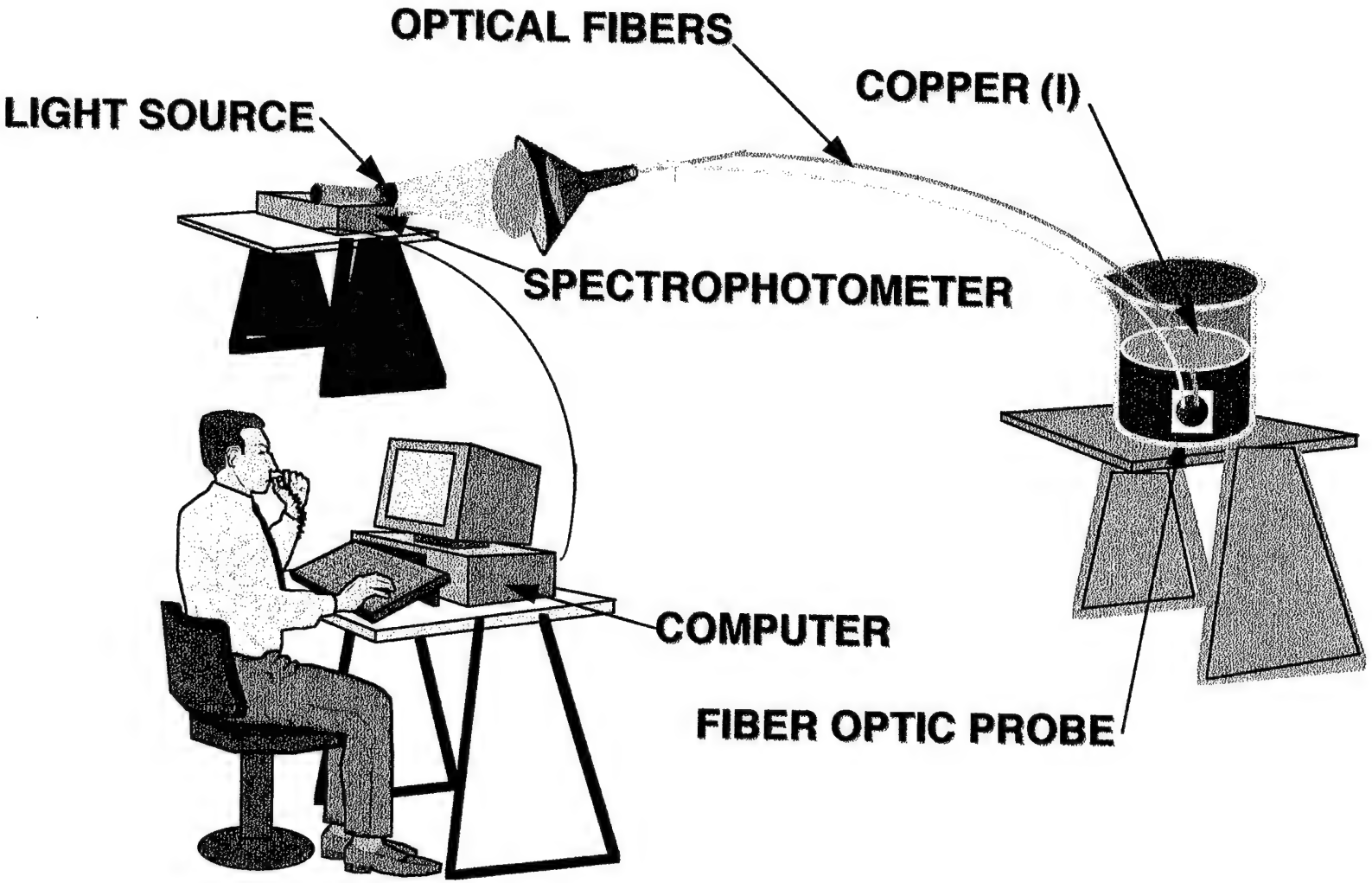
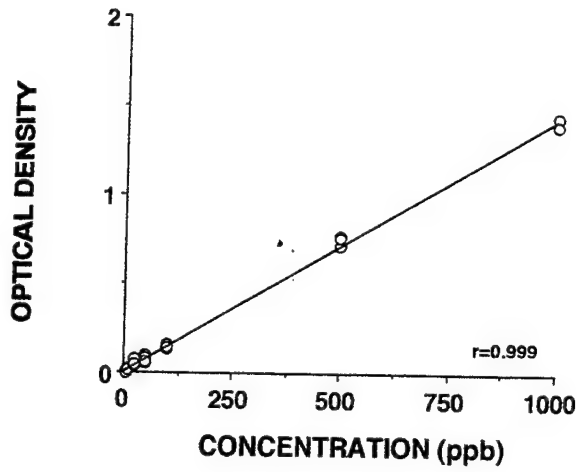
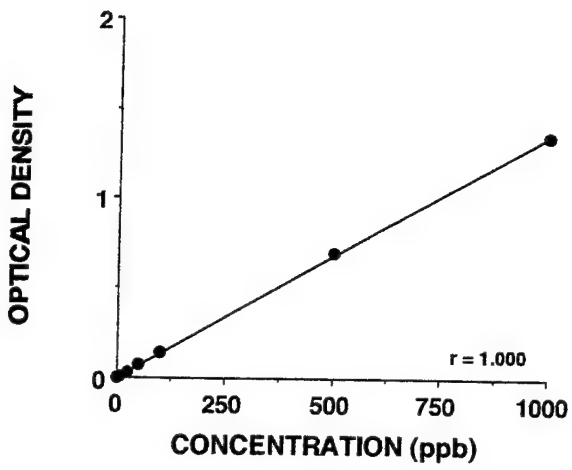

OPTICAL FIBERS
COPPER (I)
LIGHT SOURCE
SPECTROPHOTOMETER
COMPUTER
FIBER OPTIC PROBE

Figure 13.

A.



B.



C.

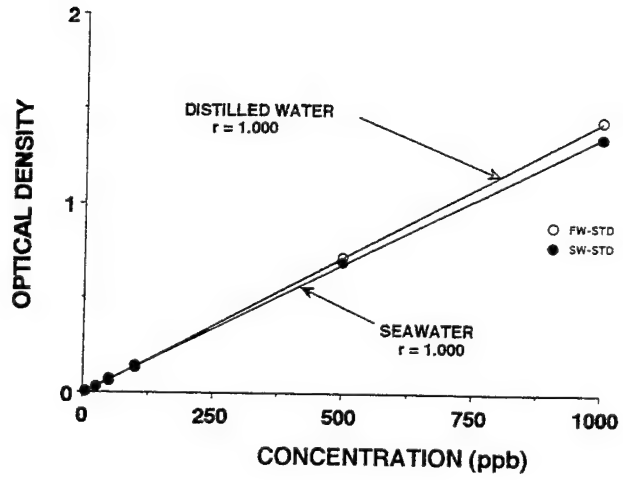
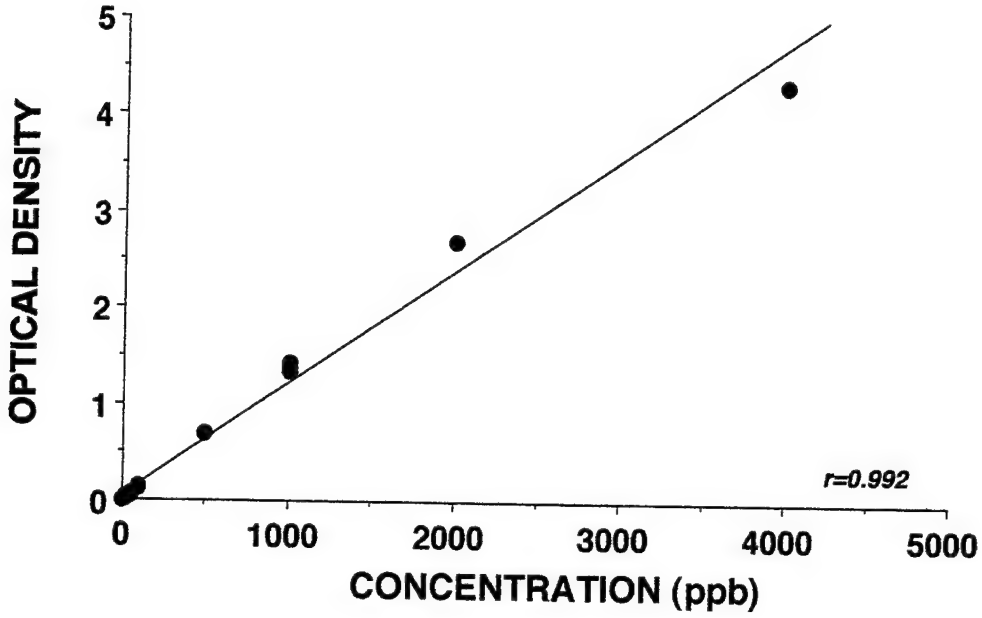


Figure 14

A.


OPTICAL DENSITY
0
1
2
3
4
5
r=0.992
0
1000
2000
3000
4000
5000
CONCENTRATION (ppb)

B.

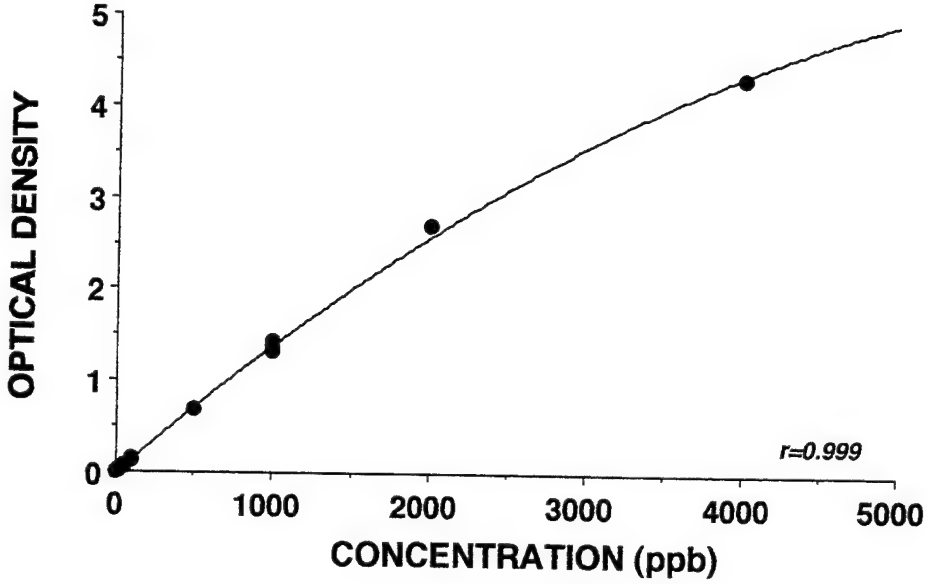

OPTICAL DENSITY
0
1
2
3
4
5
r=0.999
0
1000
2000
3000
4000
5000
CONCENTRATION (ppb)

Figure 15.

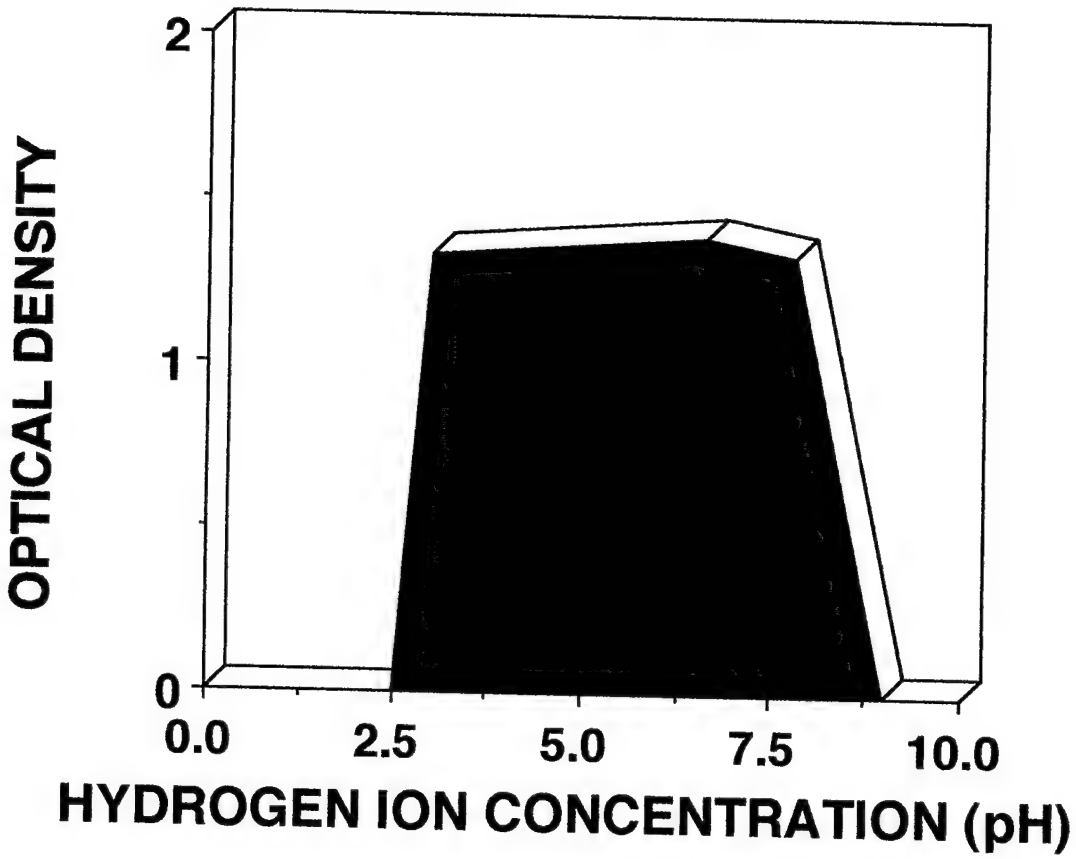
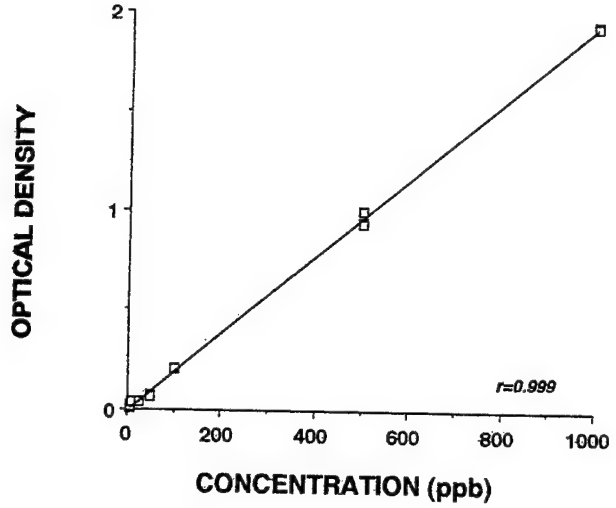
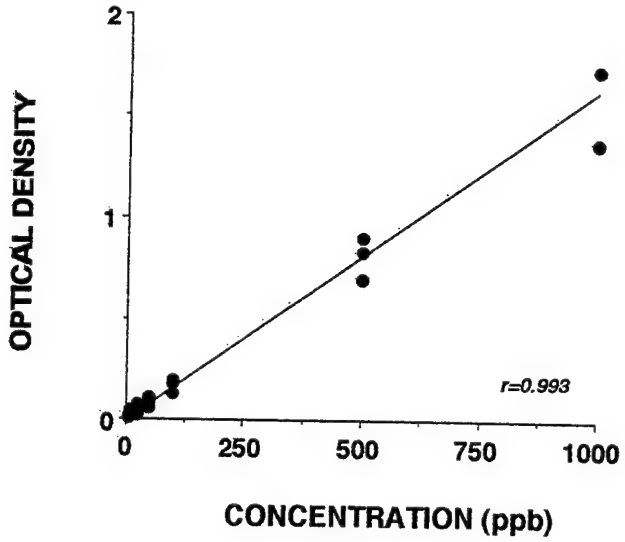

OPTICAL DENSITY
2
1
0
0.0
2.5
5.0
7.5
10.0
HYDROGEN ION CONCENTRATION (pH)

Figure 16.

A.



B.



C.

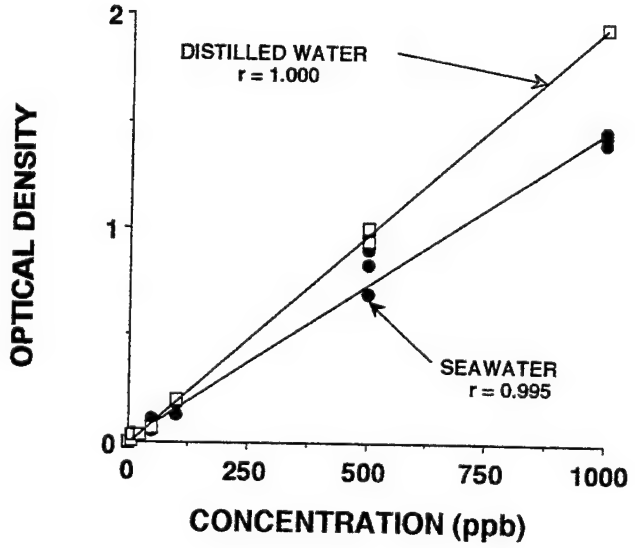


Figure 17.

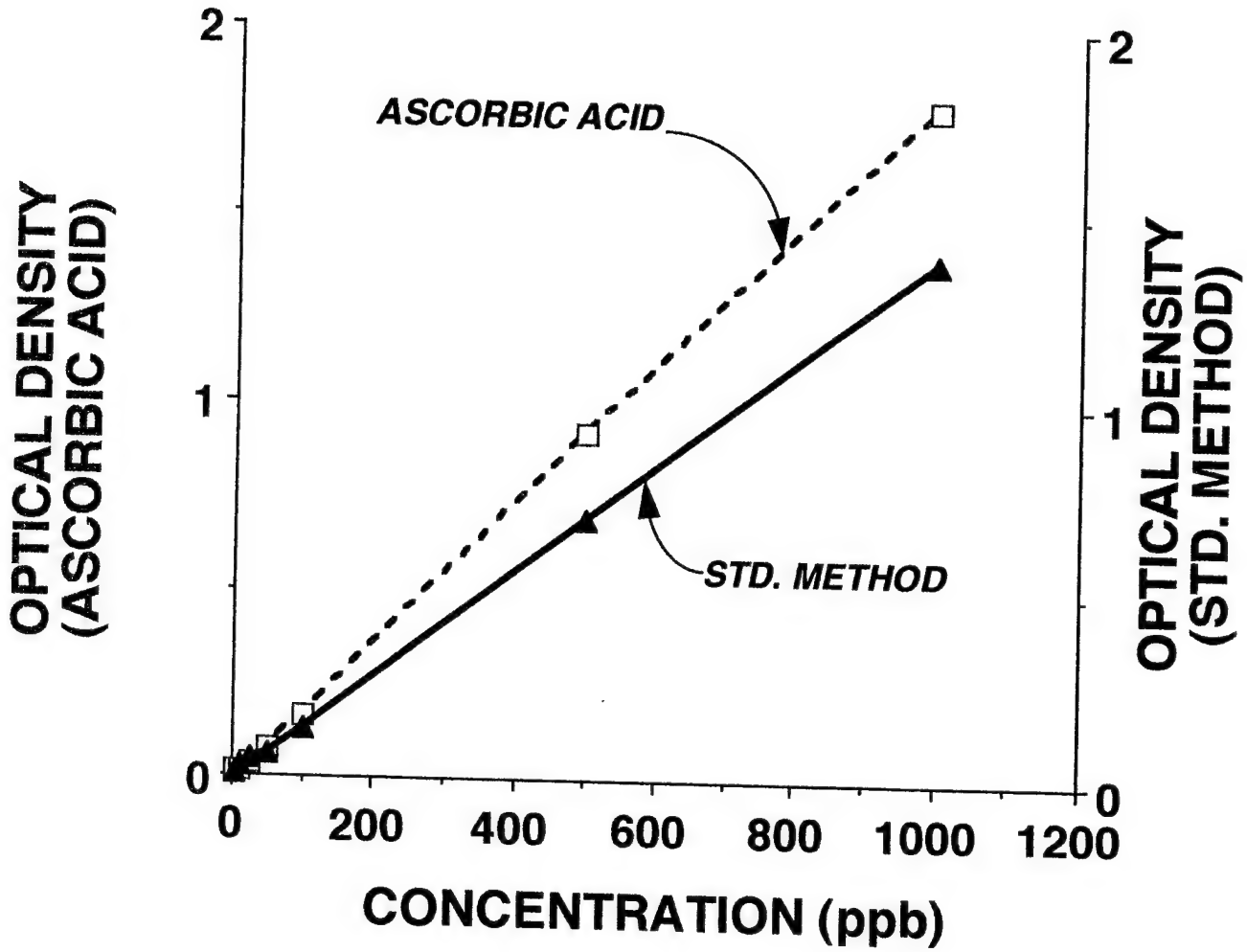

ASCORBIC ACID
STD. METHOD
OPTICAL DENSITY
(ASCORBIC ACID)
OPTICAL DENSITY
(STD. METHOD)
CONCENTRATION (ppb)
0
1
2
0
200
400
600
800
1000
1200

Figure 18.

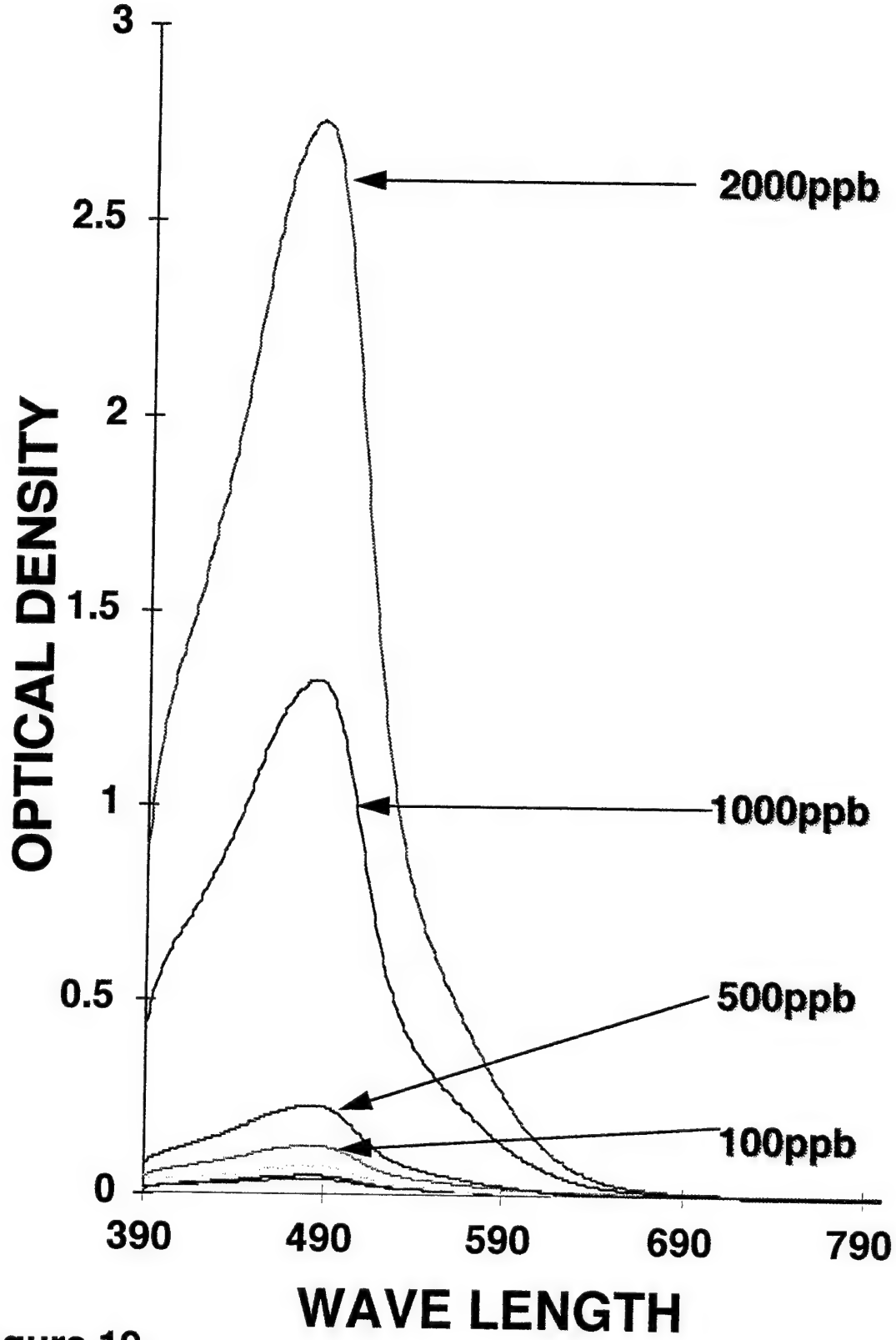
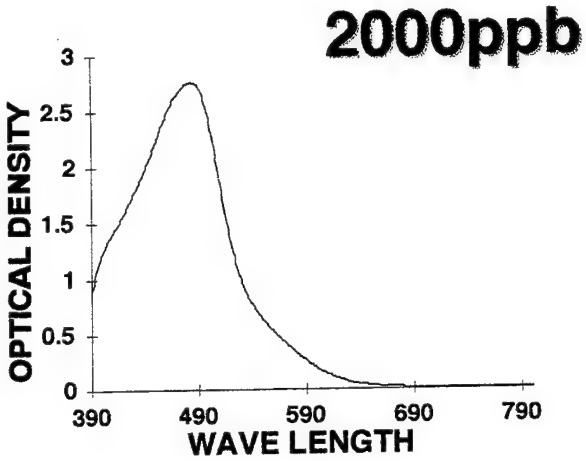
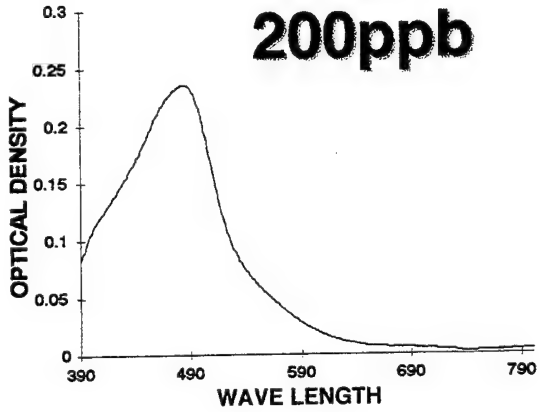

3
2.5
2
1.5
1
0.5
0
OPTICAL DENSITY
2000ppb
1000ppb
500ppb
100ppb
390
490
590
690
790
WAVE LENGTH

Figure 19.


2000ppb
OPTICAL DENSITY
3
2.5
2
1.5
1
0.5
0
390
490
590
690
790
WAVE LENGTH


200ppb
OPTICAL DENSITY
0.3
0.25
0.2
0.15
0.1
0.05
0
390
490
590
690
790
WAVE LENGTH

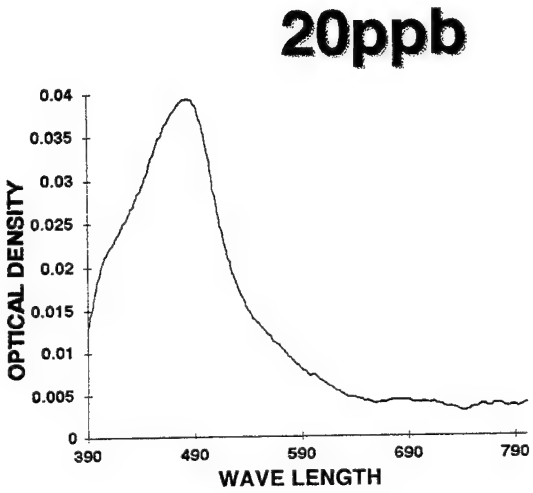
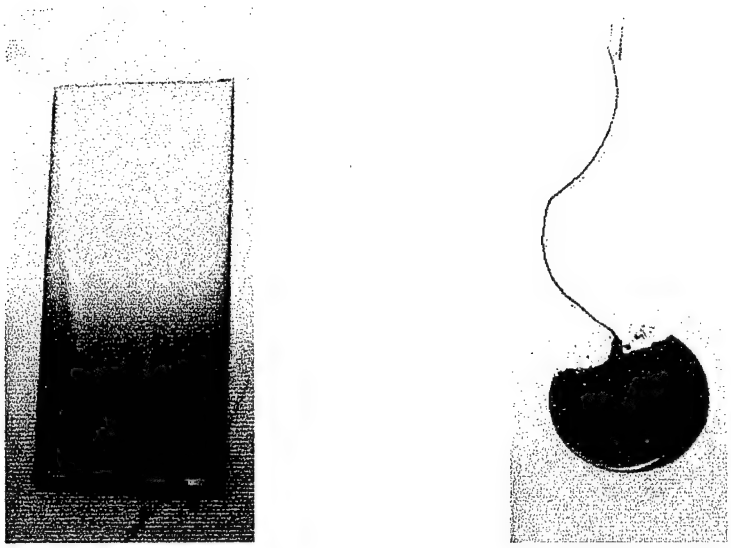

20ppb
OPTICAL DENSITY
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
390
490
590
690
790
WAVE LENGTH

Figure 20.



A. B.

Figure 21.

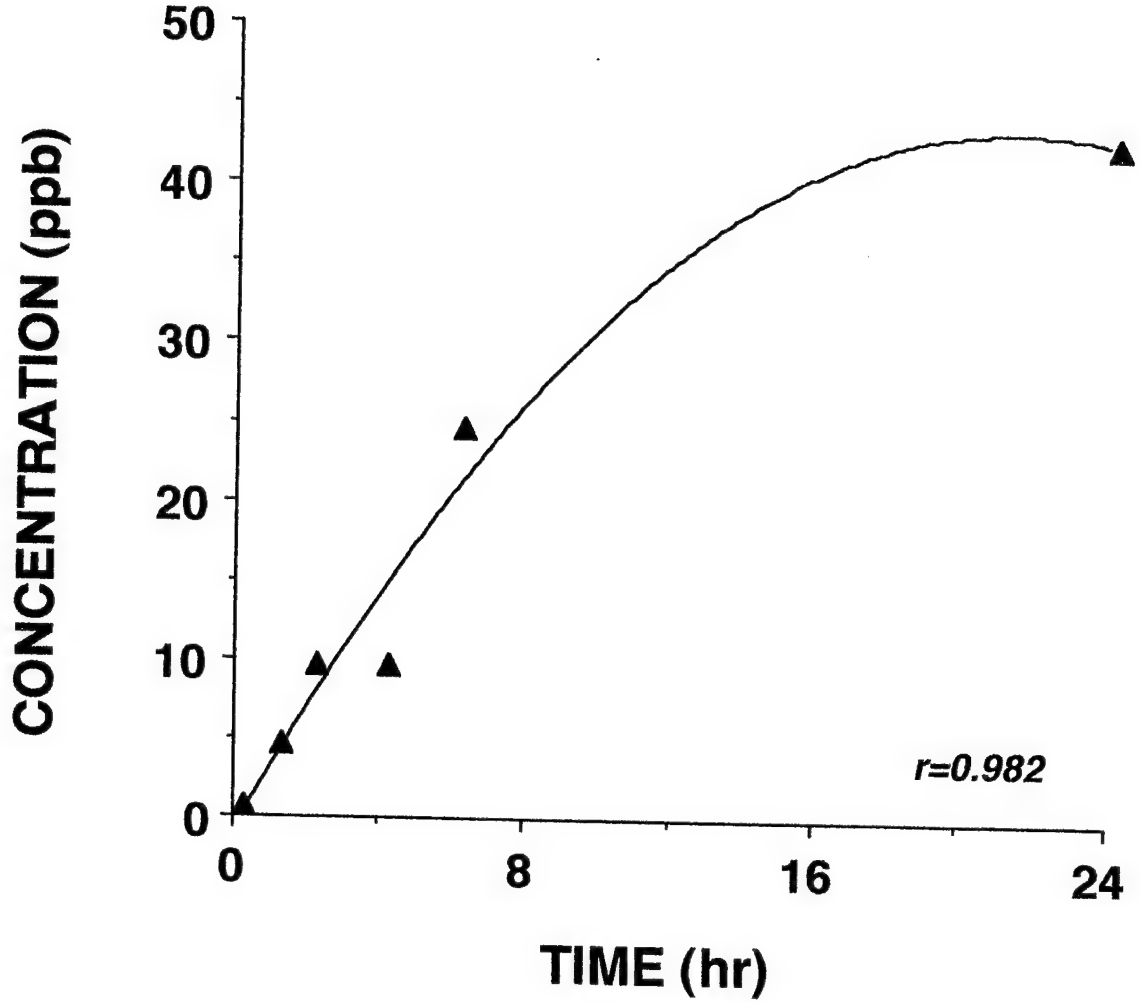


Figure 22.

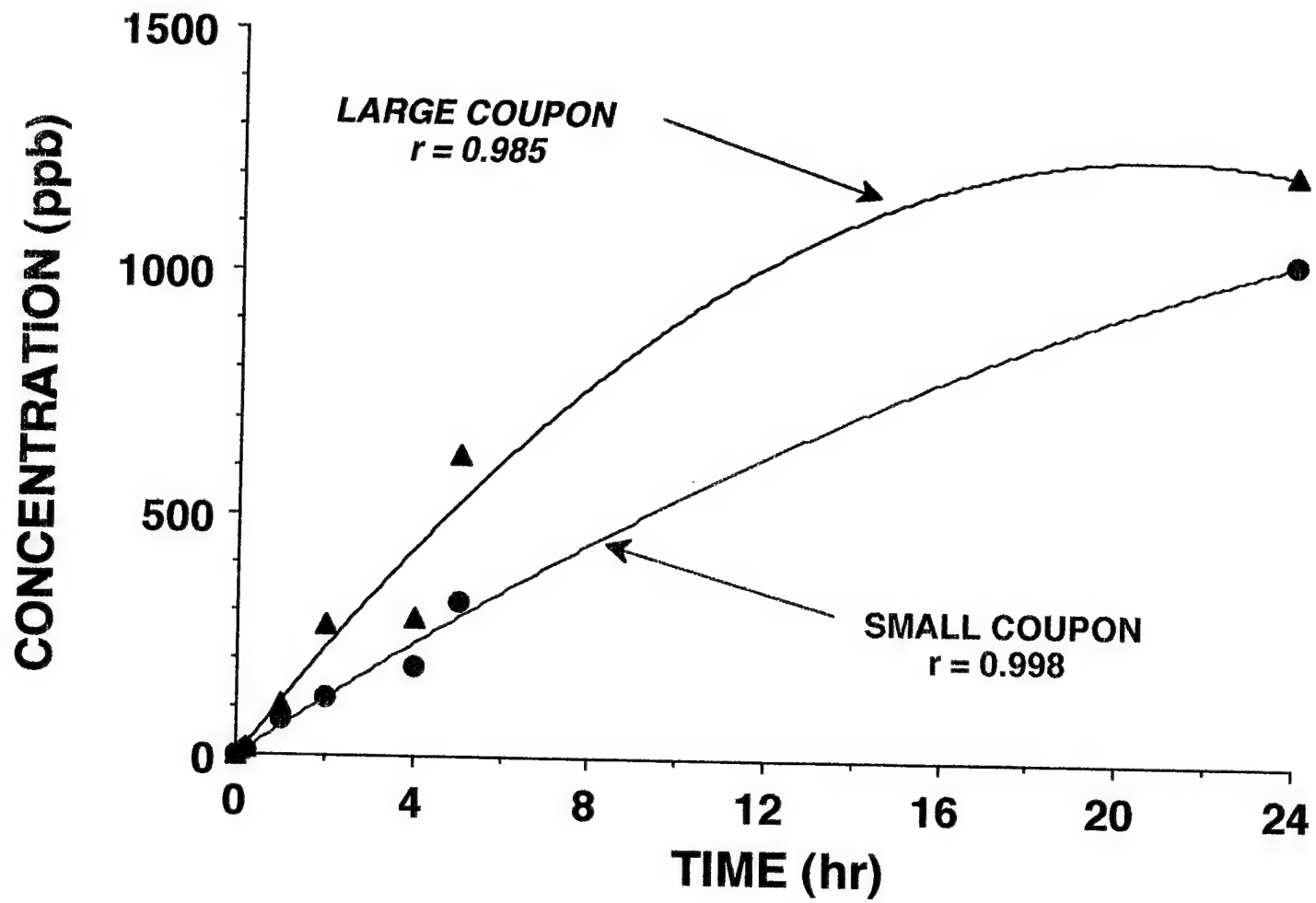

1500
1000
500
0
CONCENTRATION (ppb)
LARGE COUPON
r = 0.985
SMALL COUPON
r = 0.998
0
4
8
12
16
20
24
TIME (hr)

Figure 23.

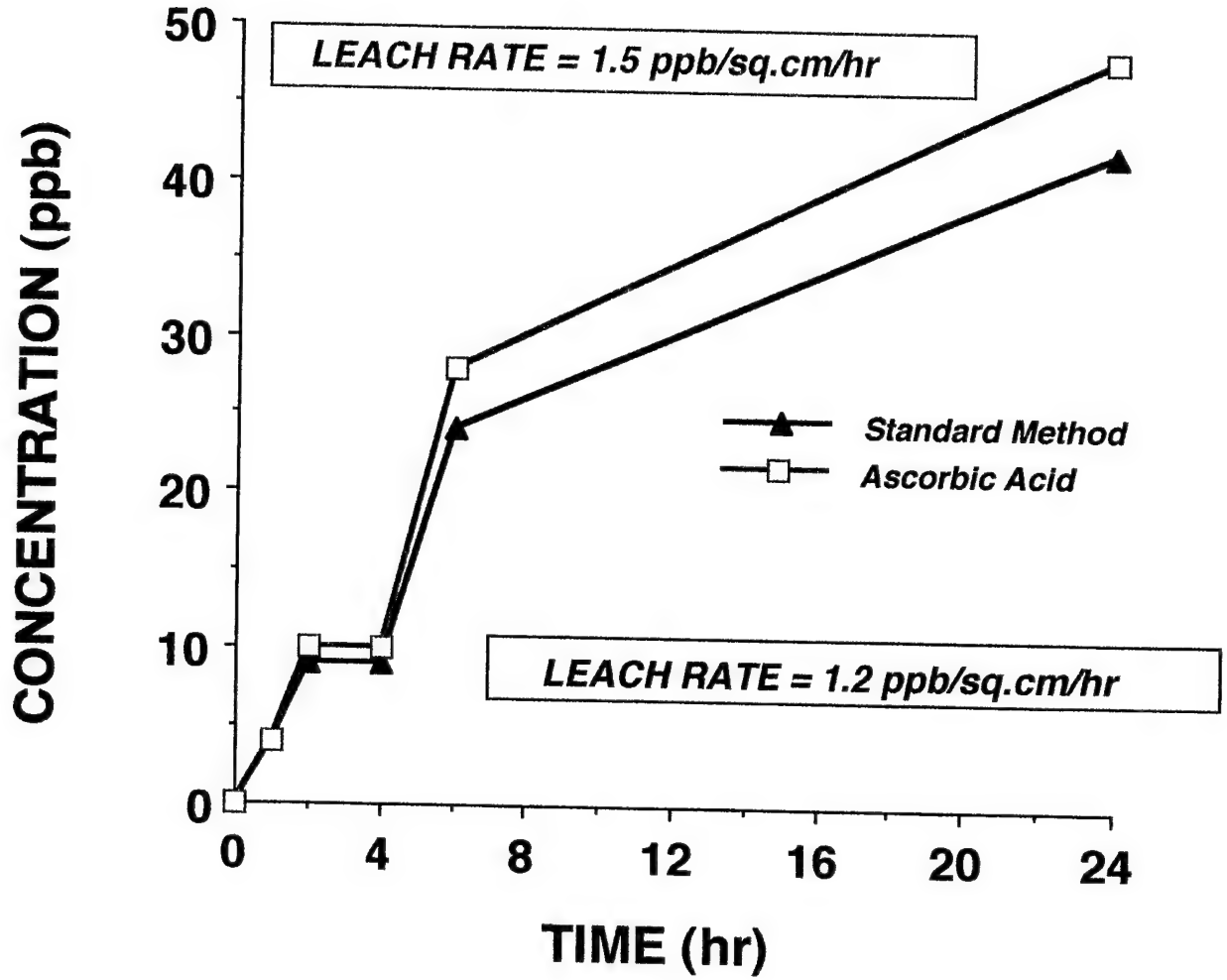

LEACH RATE = 1.5 ppb/sq.cm/hr
LEACH RATE = 1.2 ppb/sq.cm/hr
Standard Method
Ascorbic Acid
CONCENTRATION (ppb)
TIME (hr)
0
10
20
30
40
50
0
4
8
12
16
20
24

Figure 24.

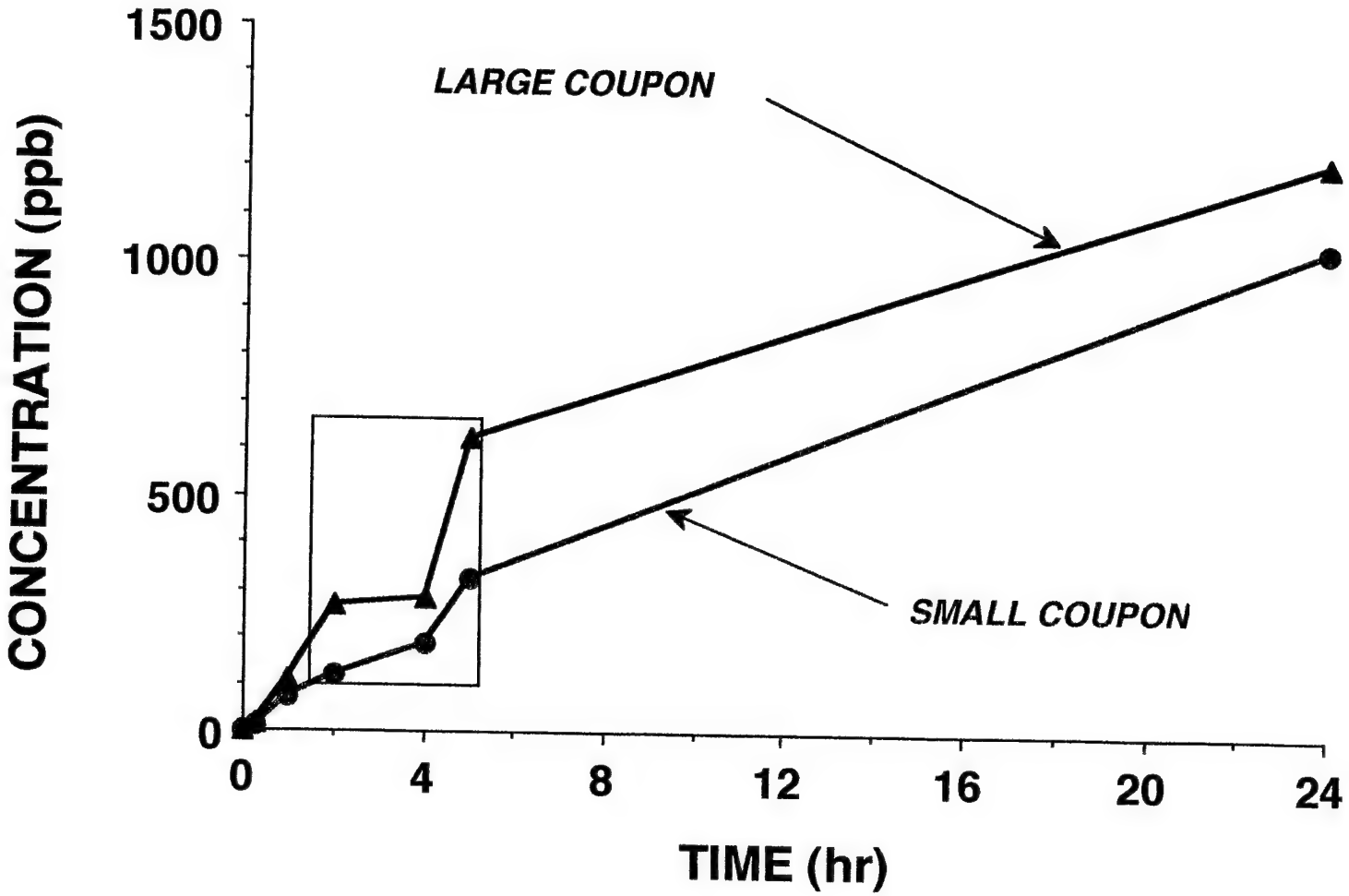
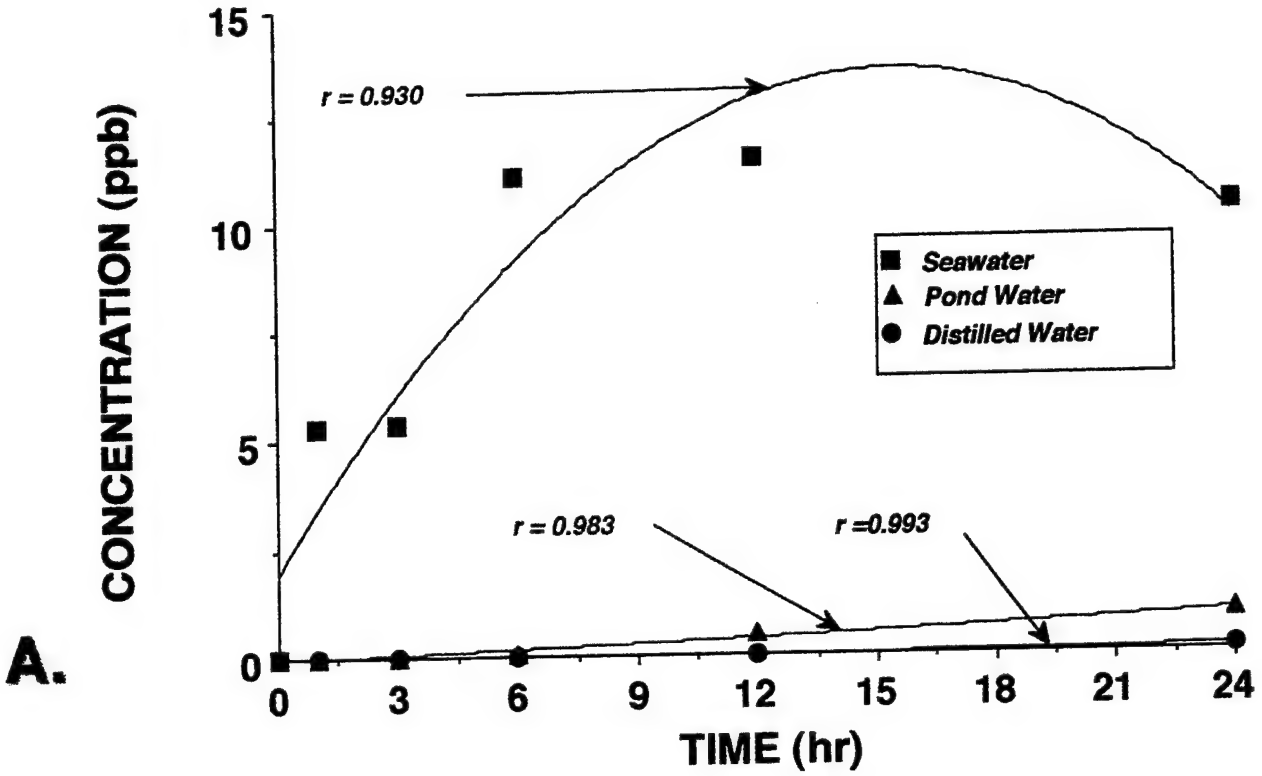

1500
1000
500
0
CONCENTRATION (ppb)
LARGE COUPON
SMALL COUPON
0
4
8
12
16
20
24
TIME (hr)

Figure 25.


A.
CONCENTRATION (ppb)
15
10
5
0
r = 0.930
r = 0.983
r =0.993
Seawater
Pond Water
Distilled Water
0
3
6
9
12
15
18
21
24
TIME (hr)

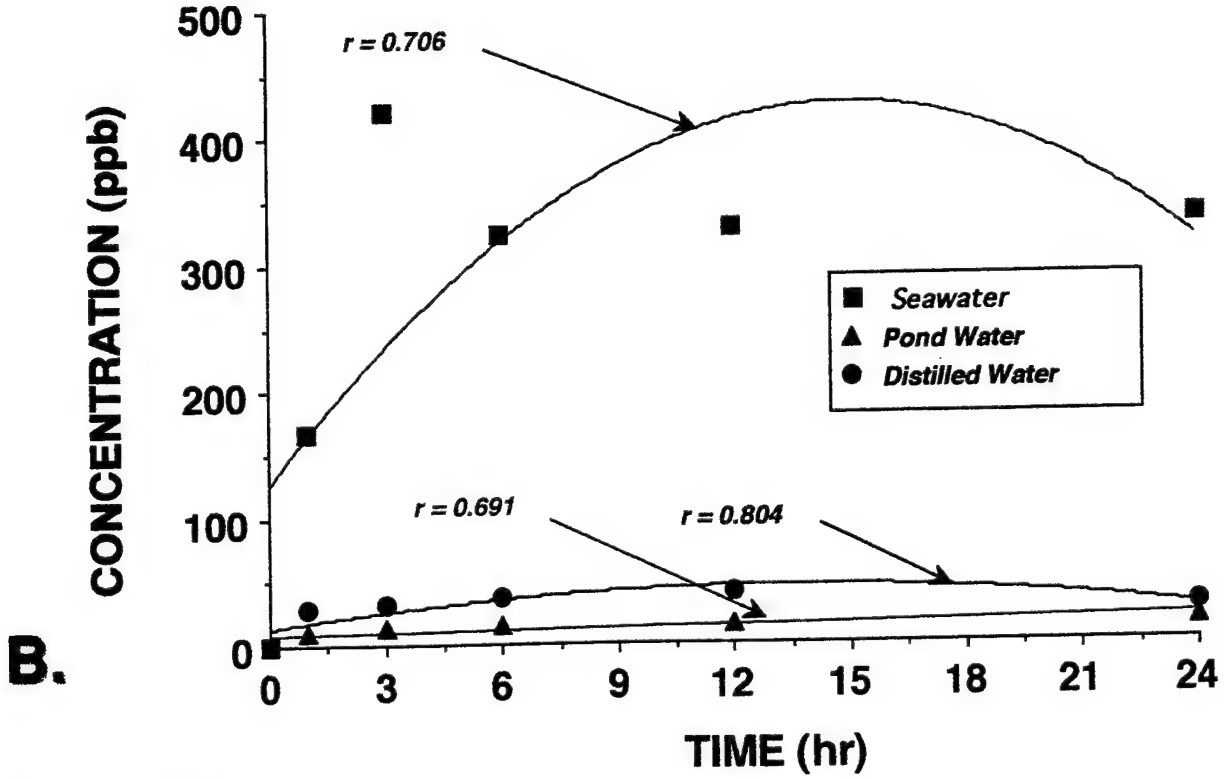

B.
CONCENTRATION (ppb)
500
400
300
200
100
0
r = 0.706
r = 0.691
r = 0.804
Seawater
Pond Water
Distilled Water
0
3
6
9
12
15
18
21
24
TIME (hr)

Figure 26.

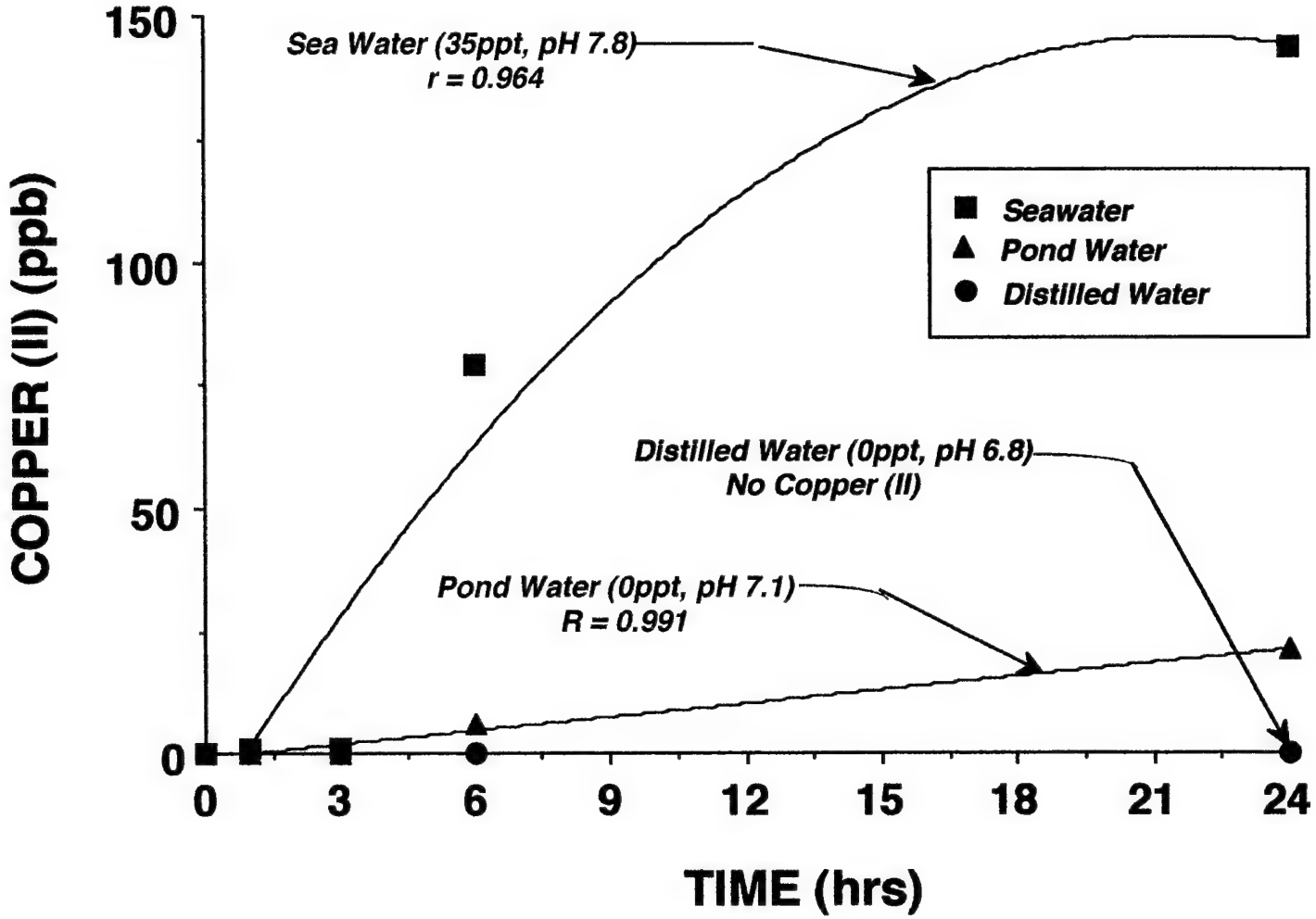

150
100
50
0
COPPER (II) (ppb)
0
3
6
9
12
15
18
21
24
TIME (hrs)
Sea Water (35ppt, pH 7.8)
r = 0.964
Seawater
Pond Water
Distilled Water
Distilled Water (0ppt, pH 6.8)
No Copper (II)
Pond Water (0ppt, pH 7.1)
R = 0.991

Figure 27.

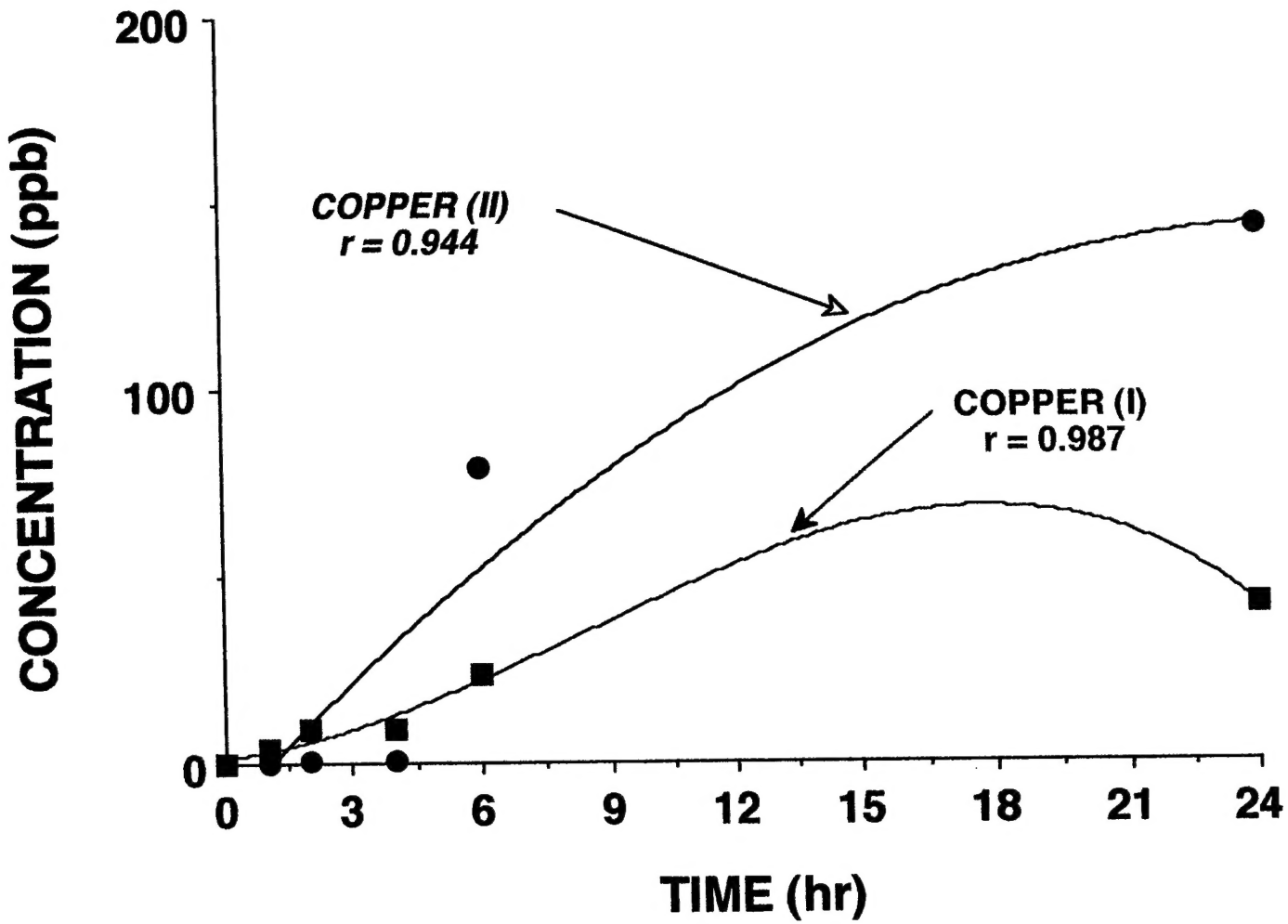

200
100
0
CONCENTRATION (ppb)
COPPER (II)
r = 0.944
COPPER (I)
r = 0.987
0
3
6
9
12
15
18
21
24
TIME (hr)

Figure 28.

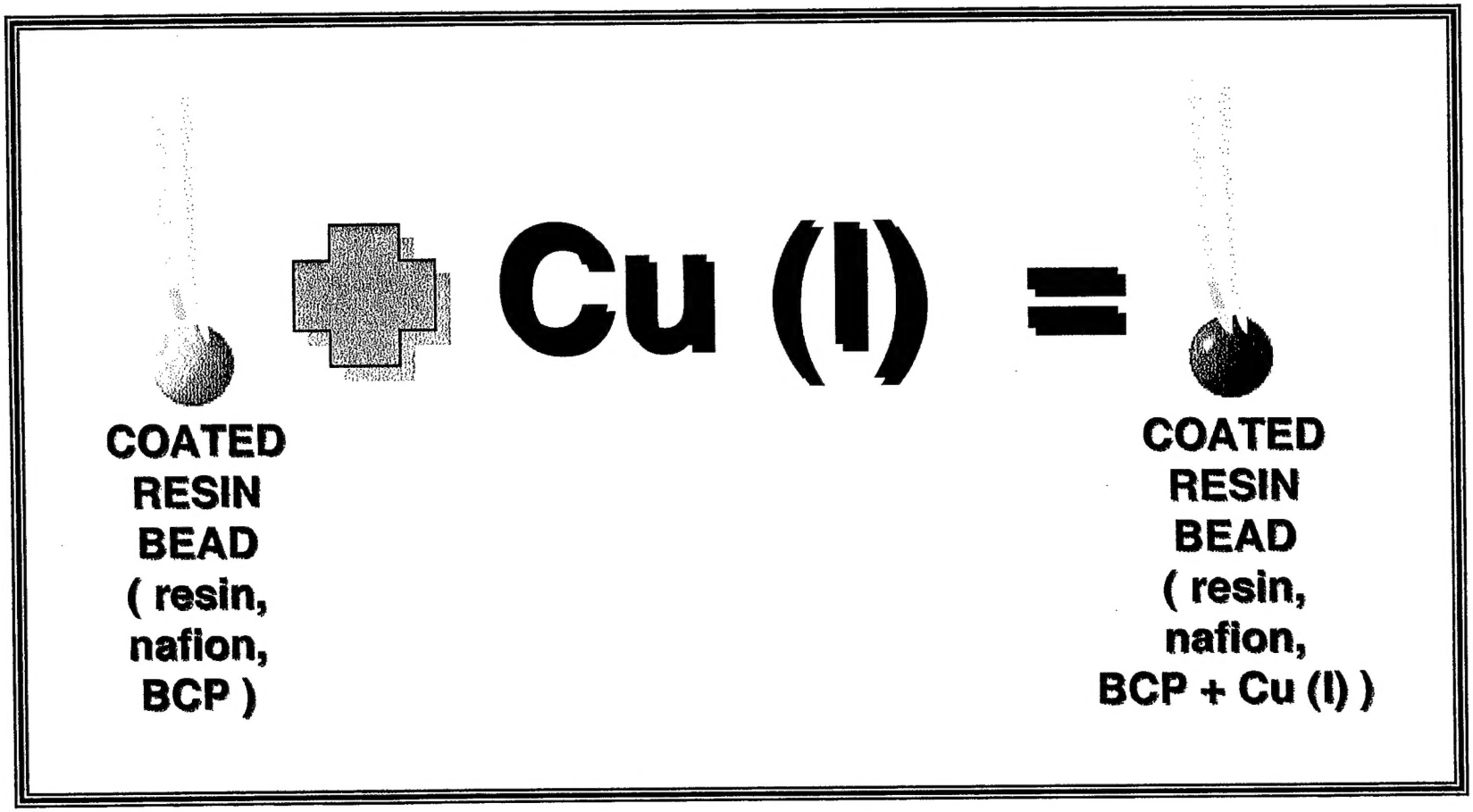

Cu (I)
COATED
RESIN
BEAD
(resin,
nafion,
BCP)
COATED
RESIN
BEAD
(resin,
nafion,
BCP + Cu (I))

Figure 29.

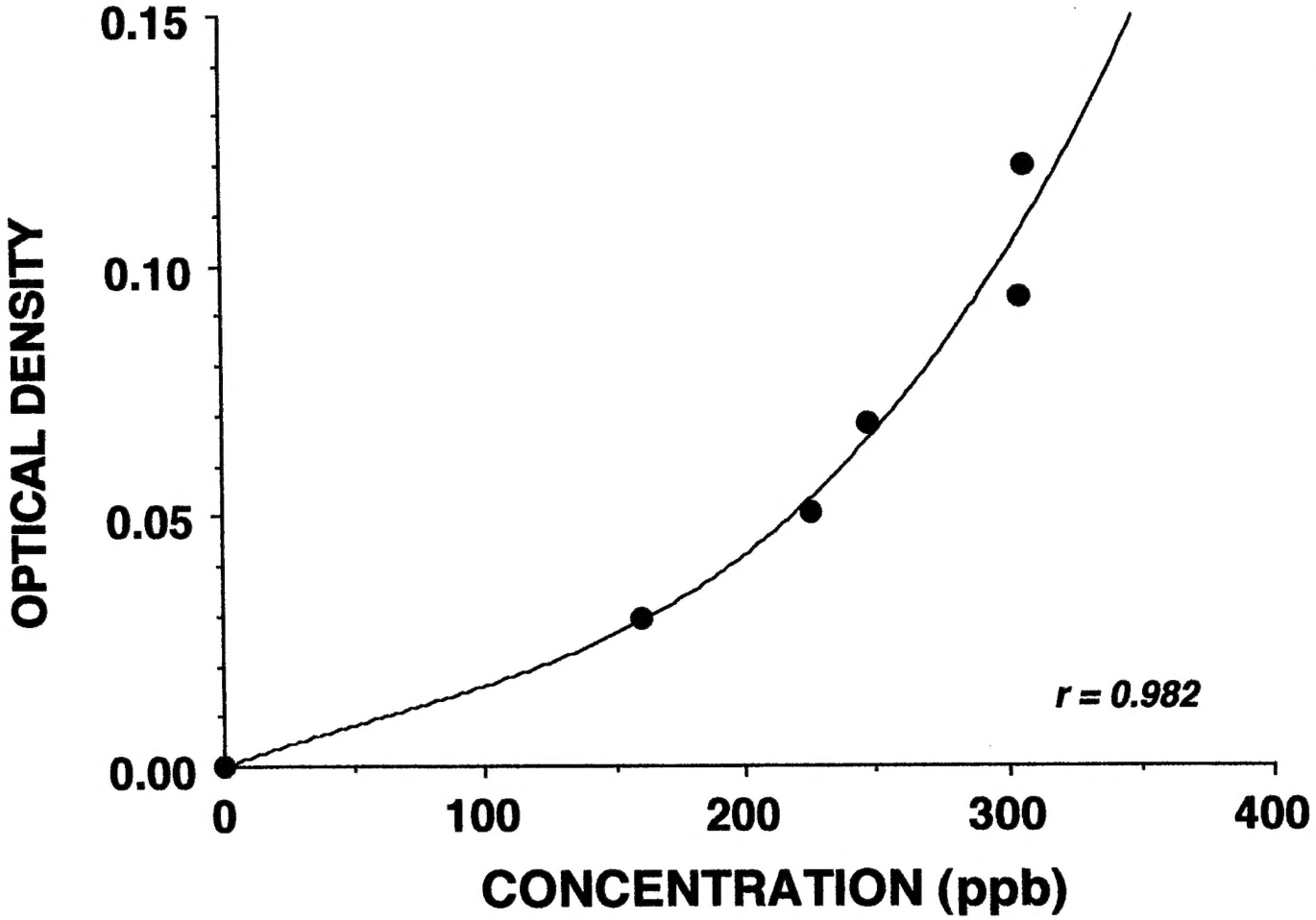

0.15
0.10
0.05
0.00
OPTICAL DENSITY
0
100
200
300
400
CONCENTRATION (ppb)
r = 0.982

Figure 30.

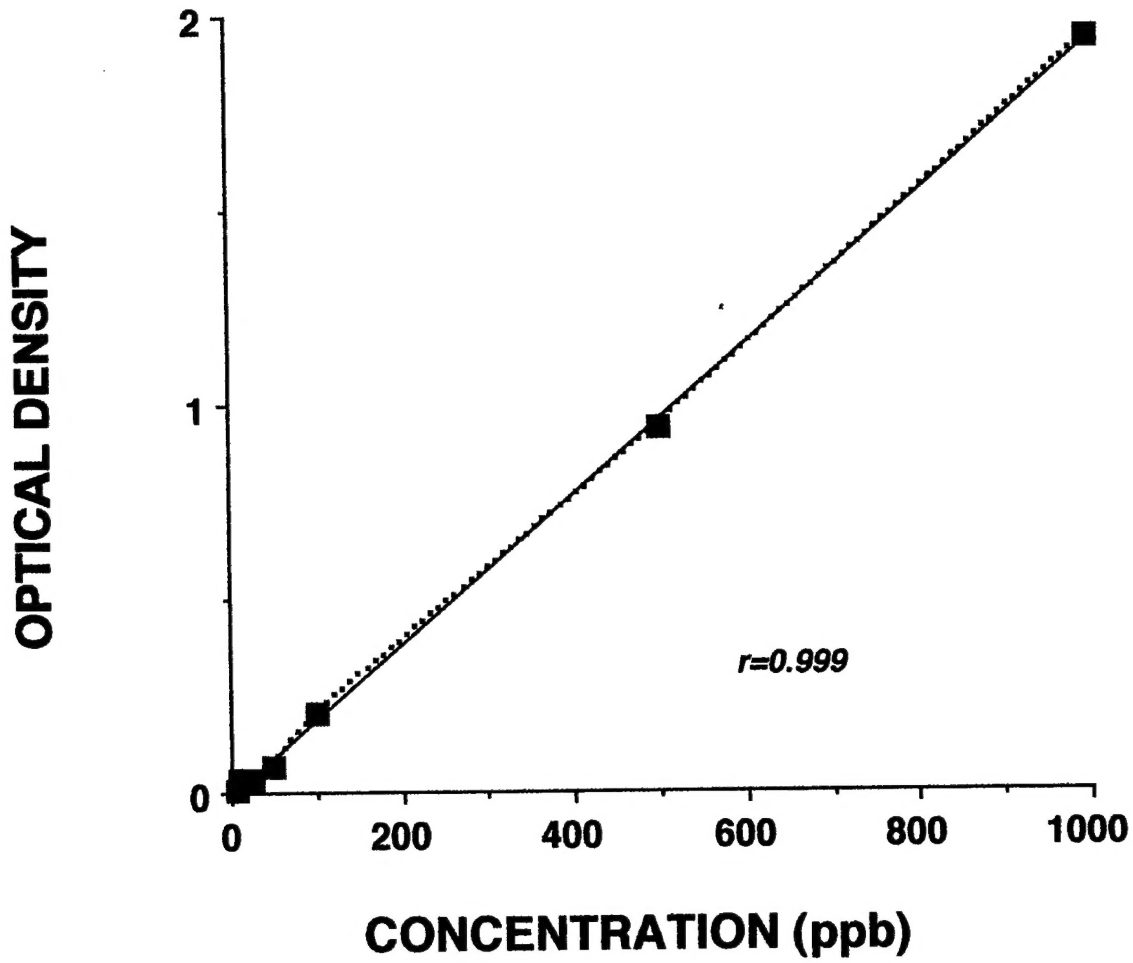

OPTICAL DENSITY
2
1
0
0
200
400
600
800
1000
CONCENTRATION (ppb)
r=0.999

Figure 31.